Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Towards the Molecular Borromean Link with Three Unequal Rings: Double-Threaded Ruthenium(II) Ring-in-Ring Complexes

Janis Veliks, Helen M. Seifert, Derik K. Frantz, Jeremy K. Klosterman, Jui-Chang Tseng, Anthony Linden and Jay S. Siegel*

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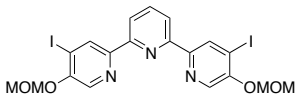
1. General

All reagents and solvents used for reactions were reagent grade and used without further purification unless otherwise noted. Anhydrous solvents were supplied from an Mbraun solvent purification system. Analytical thin-layer chromatography was performed with Macherey–Nagel POLYGRAM SIL N-HR/UV254 or ALOX N/UV254. Flash silica gel column chromatography was performed with Merck silica gel 60 (particle size 0.040–0.063 mm). Flash alumina column chromatography was performed with deactivated (5% water) Fluka alumina (particle size 0.05–0.15 mm, pH 7.0±0.5). Melting points were recorded on a Büchi B-540 melting point apparatus. For characterization purposes, proton nuclear magnetic resonance (^{1}H-NMR) spectra were all recorded on Bruker instruments (AV2- 400 at 400 MHz, AV-500 at 500 MHz, and AV-600 at 600 MHz). Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.26), $CDHCl_2$ (δ 5.31), CD_2HCN (δ 1.94), DMSO-d_6 (δ 2.50), or acetone-d_6 (δ 2.05). Multiplicity and shape are indicated by one or more of the following abbreviations: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); dd (doublet of doublets); td (triplet of doublets); m (multiplet); br (broad). Carbon-13 nuclear magnetic resonance (^{13}C- NMR) spectra were recorded on Bruker instruments (AV2-400 at 100 MHz, AV-500 at 125 MHz, and AV-600 at 150 MHz). Chemical shifts are reported relative to $CDCl_3$ (δ 77.2), CD_2Cl_2 (δ 53.8), acetone-d_6 (δ 29.8), CD_3CN (δ 1.3), or DMSO-d_6 (δ 39.5). Infrared spectroscopic data were recorded on NaCl plates as thin films, as KBr pellets or neat sample on a Perkin Elmer Spectrum One (PE) or Jasco FT/IR-4100 spectrophotometer. The intensities are given as follows: *s* = strong, *m* = medium, and *w* = weak. The diffraction data for **9a** were collected using a Nonius KappaCCD diffractometer with MoKα radiation (λ = 0.71073 Å), while the data for **13** were collected by Dr. Philip Pattison on the Swiss Norwegian Beamlines at the European Synchrotron Radiation Facility. High-resolution electrospray mass spectra (HR-ESI MS) were recorded on a Bruker maXis (QTOF-MS) instrument.

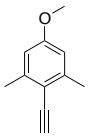
2. Experimental procedures

4,4′′-diiodo-5,5′′-bis(methoxymethoxy)-2,2′:6′,2′′-terpyridine (2)



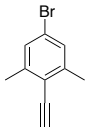
The compound **2** was synthesized according to a procedure reported in literature[1].

2-ethynyl-5-methoxy-1,3-dimethylbenzene (3a)



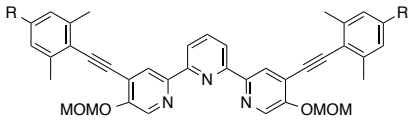
The compound **3a** was synthesized according to a procedure reported in literature[1].

5-bromo-2-ethynyl-1,3-dimethylbenzene (3b)



The compound **3b** was synthesized according to a procedure reported in literature[2].

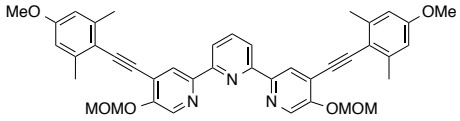
General procedure for the synthesis of 4,4′′-bis-(2-(substituted)-ethynyl)-5,5′′-bis(methoxymethoxy)-2,2′:6′,2′′-terpyridines (4)



4a R= OMe
4b R= Br

To a mixture of 4,4′′-diiodo-5,5′′-bis(methoxymethoxy)-2,2′:6′,2′′-terpyridine **2** (1.0 mmol), CuI (0.1 mmol) and $PdCl_2(PPh_3)_2$ (0.05 mmol) in degassed THF/Et_3N (10 mL/10 mL) was added acetylene **3** (amount indicated below) under N_2 atmosphere at 80 °C. The reaction mixture was heated to reflux, followed by TLC to completion, allowed to cool to room temperature and evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and then washed with 10% aqueous NH_4OH, water and brine. The organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was purified as indicated below.[3]

4,4″-bis-(2-(4-methoxy-2,6-dimethylphenyl)-ethynyl)-5,5″-bis(methoxymethoxy)-2,2′:6′,2″-terpyridine (4a)



The title compound was prepared according to the general procedure from 4,4″-diiodo-5,5″-bis(methoxymethoxy)-2,2′:6′,2″-terpyridine **2** (605 mg, 1.0 eq, 1.0 mmol) and 2-ethynyl-5-methoxy-1,3-dimethylbenzene (**3a**) (368 mg, 2.3 eq, 2.3 mmol). Heated for 8 h. Purified by silica gel column chromatography with CH_2Cl_2/MeOH (95:5) to give **4a** as an off-white solid (609 mg, 91%).

Mp: 182–183 °C.

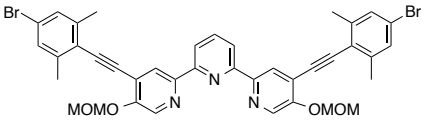
^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.65 (s, 2H), 8.57 (s, 2H), 8.38 (d, *J* = 7.9 Hz, 2H), 7.94 (t, *J* = 7.9 Hz, 1H), 6.62 (s, 4H), 5.39 (s, 4H), 3.81 (s, 6H), 3.58 (s, 6H), 2.53 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.9, 154.7, 153.3, 150.1, 142.9, 138.1, 136.9, 124.2, 123.8, 120.5, 115.0, 112.7, 96.6, 95.6, 90.7, 56.7, 55.3, 21.4.

IR (film on NaCl, cm^{-1}): 2952*w*, 2902*w*, 2836*w*, 2190*w*, 1603*m*, 1573*s*, 1484*m*, 1453*m*, 1377*m*, 1315*m*, 1303*s*, 1283*m*, 1228*m*, 1194*m*, 1155*s*, 1119*m*, 1086*m*, 1073*m*, 1058*m*, 990*s*, 921*m*, 897*m*, 853*m*, 818*m*, 732*m*, 661*w*, 602*m*.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{41}H_{40}N_3O_6$: 670.29116; found: 670.29071.

5,5″-bis-(methoxymethoxy)-4,4″-bis-((4-bromo-2,6-dimethylphenyl)ethynyl)-2,2′:6′,2″-terpyridine (4b)



The title compound was prepared according to the general procedure from 4,4″-diiodo-5,5″-bis(methoxymethoxy)-2,2′:6′,2″-terpyridine **2** (605 mg, 1.0 eq, 1.0 mmol) and 5-bromo-2-ethynyl-1,3-dimethylbenzene (**3b**) (406 mg, 2.2 eq, 2.2 mmol). Heated for 18 h. Purified by neutral Al_2O_3 (deact. with 5% w/w H_2O) column chromatography with hexane/EtOAc (gradient 3:1 to 1:1) to give **4b** as a light yellow solid (491 mg, 64%).

Mp: 181–184 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.65 (s, 2H), 8.59 (s, 2H), 8.36 (d, *J* = 7.8 Hz, 2H),

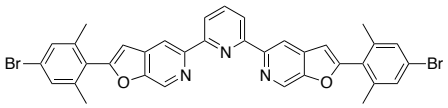
7.93 (t, J = 7.8 Hz, 1H), 7.25 (s, 4H), 5.39 (s, 4H), 3.57 (s, 6H), 2.50 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 154.8, 153.4, 150.2, 142.7, 138.1, 137.0, 130.1, 124.2, 123.0, 122.7, 121.6, 120.5, 95.5, 94.7, 92.9, 56.7, 21.0.

IR (film on NaCl, cm^{-1}): 2953*w*, 2919*w*, 2853*w*, 2211*w*, 1572*m*, 1538*w*, 1485*m*, 1454*w*, 1376*w*, 1306*w*, 1262*m*, 1202*m*, 1155*s*, 1086*m*, 1073*m*, 991*vs*, 921*w*, 902*w*, 854*w*, 838*w*, 817*m*, 777*w*, 724*w*, 606*w*.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{39}H_{34}Br_2N_3O_4$ 766.09106, found 766.09145.

2,6-bis(2-(4-bromo-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)pyridine (5a)



To a solution of 5,5″-bis-(methoxymethoxy)-4,4″-bis-((4-bromo-2,6-dimethylphenyl)ethynyl)-2,2′:6′,2″-terpyridine (**4b**) (543 mg, 1.0 eq, 0.707 mmol) in DMF (25 mL) was added 32% aq. HCl (0.347 mL, 5.0 eq, 3.54 mmol). The reaction mixture was heated to 80 °C for 20 h, then Cs_2CO_3 (10.4 g, 45 eq, 31.8 mmol) was added portion-wise. The resulting mixture was heated to 90 °C for 18 h. Evaporation of DMF gave a residue that was suspended in water (200 ml). The resulting solid was collected by filtration, washed on the filter with excess water and re-dissolved with CH_2Cl_2 (200 ml) into a clean flask. Evaporation of solvent gave a crude product, which was dissolved in a minimum amount of CH_2Cl_2, introduced on a short neutral Al_2O_3 (deact. with 5% w/w H_2O) chromatographic column and eluted with hexane:EtOAc 3:1. Evaporation of the product fractions gave **5a** (414 mg, 86%) as an off-white solid.

Mp: 283.3–284.0 °C.

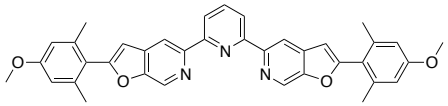
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.95 (s, 4H, two signals overlapping), 8.47 (d, J = 7.8 Hz, 2H), 7.98 (t, J = 7.8 Hz, 1H), 7.35 (s, 4H), 6.84 (s, 2H), 2.26 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 157.9, 155.9, 152.6, 150.5, 140.7, 138.1, 136.2, 132.7, 130.8, 128.8, 124.1, 120.6, 113.7, 106.8, 20.5.

IR (film on NaCl, cm^{-1}): 2957*w*, 2924*w*, 2853*w*, 1604*m*, 1571*s*, 1447*vs*, 1398*m*, 1307*w*, 1291*w*, 1251*w*, 1239*w*, 1145*m*, 1112*w*, 1075*w*, 1010*m*, 914*m*, 856*m*, 824*s*, 802*w*, 733*m*, 651*w*.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{35}H_{26}Br_2N_3O_2$: 678.03863; found: 680.03747.

2,6-bis-(2-(4-methoxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)pyridine (5b)



To a suspension of **4a** (478 mg, 1.0 eq, 0.747 mmol) in DMF (30 mL) was added 32% aq. HCl (0.37 mL, 5.0 eq, 3.7 mmol). After heating the reaction mixture to 80 °C for 24 h, Cs_2CO_3 (10.9 g, 45 eq, 33.6 mmol) was added. The resulting mixture was heated to 90 °C for 30 h. Evaporation of DMF gave a residue that was suspended in water (200 ml). The resulting solid was collected by filtration, washed on the filter with excess water, hexane (4 mL) and re-dissolved with CH_2Cl_2 (200 ml) into a clean flask. Evaporation of solvent gave a crude product, which was dissolved in a minimum amount of CH_2Cl_2, introduced on a short neutral Al_2O_3 (deact. with 5% w/w H_2O) chromatographic column and eluted with hexane:EtOAc 3:1. The solvent was evaporated under reduced pressure to give the desired product **5b** (429 mg, 99%) as an off-white solid.

Mp: 228.0–232.0 °C.

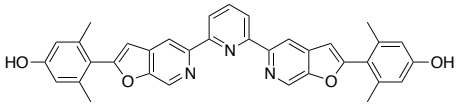
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.95 (d, *J* = 0.8 Hz, 2H), 8.93 (s, 2H), 8.46 (d, *J* = 7.8 Hz, 2H), 7.98 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 0.7 Hz, 2H), 6.72 (s, 4H), 3.85 (s, 6H), 2.27 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 160.5, 159.3, 156.0, 152.5, 150.2, 140.3, 138.0, 136.5, 132.5, 122.3, 120.5, 113.5, 113.3, 106.4, 55.4, 21.0.

IR (Neat, cm^{-1}): 2958*w*, 2838*w*, 1606*s*, 1570*m*, 1463*m*, 1446*s*, 1398*m*, 1318*s*, 1286*m*, 1268*w*, 1242*w*, 1194*m*, 1152*s*, 1069*m*, 1035*w*, 1008*w*, 941*w*, 9001*w*, 857*w*, 823*m*, 738*w*, 653*w*.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{32}N_3O_4$: 582.23873; found: 582.23864.

2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine (5c)



Compound **5b** (0.052 g, 1.0 eq, 0.089 mmol) and pyridine hydrochloride (0.50 g, 50 eq, 4.5 mmol) were placed in a sealed microwave tube and the mixture was heated under the microwave to 190 °C for 2 x 2 min. After cooling to room temperature, the mixture was suspended in H_2O, the solid was filtered off and washed with H_2O and aqueous NH_4OH (12%) and dried under vacuum to yield **5c** (0.042 g, 85%) as a

yellowish solid.

Mp: (decomp.) 285–295 °C.

^{1}H NMR (500 MHz, DMSO-d_6, δ): 9.71 (s, 2H), 9.04 (s, 2H), 8.99 (d, *J* = 0.9 Hz, 2H), 8.45 (d, *J* = 7.9 Hz, 2H), 8.09 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 0.7 Hz, 2H), 6.63 (s, 4H), 2.18 (s, 12H).

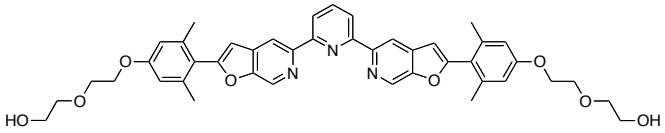
^{13}C NMR (125 MHz, DMSO-d_6, δ): 159.2, 158.4, 155.2, 151.8, 149.0, 139.5, 138.3, 136.2, 132.3, 120.1, 119.9, 114.6, 113.0, 106.5, 20.4.

IR (KBr, cm^{-1}): 3451*br*, 2959*w*, 2935*w*, 1836*w*, 1606*s*, 1570*m*, 1462*m*, 1447*m*, 1398*m*, 1384*w*, 1321*m*, 1282*m*, 1266*w*, 1197*w*, 1154*s*, 1069*m*, 1033*w*, 1012*w*, 998*w*, 942*w*, 901*w*, 856*w*, 826*m*, 738*w*, 653*w*, 599*w*, 523*w*.

MS (ESI) m/z: 554.3 ([M + H]$^+$); 576.2 ([M + Na]$^+$).

HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{35}H_{28}N_3O_4$: 554.20743; found: 554.20734.

2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)diethanol (5d)



To a mixture of 2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine (**5c**) (100 mg, 1.0 eq, 0.181 mmol) and anhydrous Cs_2CO_3 (177 mg, 3.0 eq, 0.542 mmol) in dry DMF (4 mL) under N_2 atmosphere was added 2-(2-chloroethoxy)ethanol (0.055 mL, 2.9 eq, 0.521 mmol). The reaction mixture was heated to 100 °C for 18 h. The reaction mixture was allowed to cool to room temperature and DMF was evaporated under reduced pressure. The resulting residue was treated with water and extracted with CH_2Cl_2 (4 × 80 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated. The resulting crude product was purified by silica gel column chromatography (eluent gradient CH_2Cl_2:MeOH 100:0 to 95:5) to give desired compound **5d** (96 mg, 72%) as a sticky amorphous solid. (Treatment of the product with Et_2O and evaporation under reduced pressure helped to obtain an easily transferable, flocky solid).

Mp: 85.6–86.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.94 (d, *J* = 1.0 Hz, 2H), 8.93 (t, *J* = 0.9 Hz, 2H), 8.45 (d, *J* = 7.9 Hz, 2H), 7.97 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 0.9 Hz, 2H), 6.74 (s,

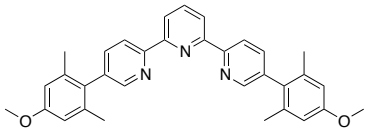
4H), 4.21-4.18 (m, 4H), 3.91-3.89 (m, 4H), 3.81-3.76 (m, 4H), 3.72-3.69 (m, 4H), 2.26 (s, 12H), 2.20-2.17 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.6, 159.3, 155.9, 152.5, 150.2, 140.4, 138.0, 136.5, 132.4, 122.6, 120.5, 113.9, 113.6, 106.5, 72.7, 69.8, 67.5, 61.9, 21.0.

IR (film on NaCl, cm^{-1}): 3356*br*, 2925*m*, 2866*w*, 1607*s*, 1570*m*, 1449*s*, 1400*s*, 1318*m*, 1285*w*, 1161*m*, 1132*m*, 1070*w*, 1007*w*, 907*m*, 858*w*, 824*m*, 733*m*, 642*w*.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{43}H_{44}N_3O_8$: 730.31229; found: 730.31240.

5′,5″-bis-(4-methoxy-2,6-dimethylphenyl)-2,2′:6′,2″-terpyridine (6a)

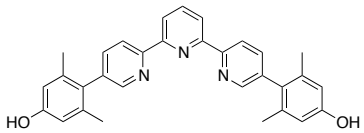


Prepared according to the known procedure[4].

To a solution of 2-bromo-5-(4-methoxy-2,6-dimethylphenyl)-pyridine[4] (1.49 g, 2.0 eq, 5.11 eq) in anhydrous THF (72 ml) under N_2 atmosphere was added dropwise 2.5 M *n*-butyllithium in hexane (2.14 mL, 2.09 eq, 5.35 mmol) over 10 min at -78 °C. To this mixture was added dropwise precooled to 0 °C a solution of $ZnCl_2$ (0.729 mg, 2.09 eq, 5.35 mmol. *Before using, $ZnCl_2$ was heated to 400 °C under high vacuum until molten and dried for an additional 3h at room temperature*) in anhydrous THF (20 mL). The reaction mixture was allowed to warm up to room temperature. Subsequently, a solution of 2,6-dibromopyridine (0.606 g, 1.0 eq, 2.56 mmol) and $Pd(PPh_3)_4$ (0.296 g, 0.1 eq, 0.256 mmol) in anhydrous THF (20 mL) was added dropwise over 10 min. The reaction mixture was heated to reflux for 20 h, allowed to cool to room temperature, and placed in a freezer. The white precipitate was filtered, washed with cold THF and dried. The white precipitate was dissolved in dichloromethane and extracted vigorously with saturated aqueous EDTA, and basified with aq. $NaHCO_3$. The organic layer was separated, dried over $MgSO_4$, filtered, and evaporated to afford the desired product **6a** (0.893 g, 70 %) as a white crystalline solid.

Analytical data consistent with literature values.[4]

4,4′-((2,2′:6′,2″-terpyridine)-5,5″-diyl)bis(3,5-dimethylphenol) (6b)



5′,5″-Bis-(4-methoxy-2,6-dimethylphenyl)-2,2′:6′,2″-terpyridine (**6a**) (0.893 g, 1.0 eq, 1.78 mmol) and pyridine hydrochloride (4.0 g, 19 eq, 35 mmol) were placed in a sealed microwave tube and the mixture was heated in the microwave reactor to 190 °C for 10 min. After cooling to room temperature, the mixture was suspended in H_2O, the solid was filtered off, washed with H_2O and aqueous NH_4OH (10%), and dried under vacuum to yield **6b** (0.701 g, 83 %) as a yellowish solid.

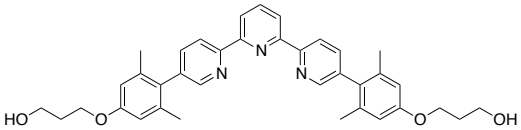
Mp: >250 °C dec.

^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.33 (s, 2H), 8.70 (dd, J = 8.1, 0.9 Hz, 2H), 8.52 – 8.44 (m, 4H), 8.13 (t, J = 7.8 Hz, 1H), 7.80 (dd, J = 8.1, 2.3 Hz, 2H), 6.60 (s, 4H), 1.98 (s, 12H).

^{13}C NMR (100 MHz, DMSO-d_6, δ): 156.7, 154.8, 153.3, 150.0, 138.7, 138.5, 136.9, 136.7, 128.2, 120.4, 120.3, 114.4, 20.7.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{28}N_3O_2$: 474.21760; found: 474.21690. *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{27}N_3NaO_2$: 474.21760; found: 496.19866.

3,3′-(((2,2′:6′,2″-terpyridine)-5,5″-diylbis(3,5-dimethyl-4,1-phenylene))bis(oxy))bis(propan-1-ol) (6c)



To a mixture of 4,4′-((2,2′:6′,2″-terpyridine)-5,5″-diyl)bis(3,5-dimethylphenol) (**6b**) (350 mg, 1.0 eq, 0.739 mmol) and dry Cs_2CO_3 (723 mg, 3.0 eq, 2.22 mmol) in anhydrous DMF (14 mL) under N_2 atmosphere was added 3-chloropropan-1-ol (0.137 mL, 2.2 eq, 1.63 mmol). The reaction mixture was heated to 100 °C for 20 h, solvent evaporated and the crude residue was directly purified by Al_2O_3 (deact. with 5% w/w H_2O) column chromatography (gradient CH_2Cl_2:MeOH 100:0 to 96:4) to give the desired product **6c** (298 mg, 68%) as a yellowish amorphous solid.

Mp: 90–96 °C.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.72 (d, J = 8.1 Hz, 2H), 8.52 (s, 2H), 8.51 (d, J = 7.8 Hz, 2H), 8.01 (t, J = 7.8 Hz, 1H), 7.68 (dd, J = 8.0, 2.2 Hz, 2H), 6.73 (s, 4H), 4.16 (t,

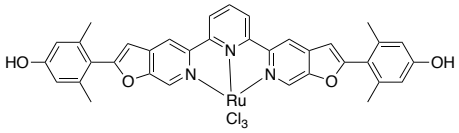
J = 6.0 Hz, 4H), 3.88 (t, *J* = 6.0 Hz, 4H), 2.08 (s, 12H, overlapping signals), 2.08 (quint, *J* = 6.0 Hz, 4H, overlapping signals).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 158.3, 155.4, 154.6, 150.0, 138.5, 138.2, 138.0, 136.8, 130.6, 121.0, 121.0, 113.7, 65.8, 60.5, 32.2, 21.3.

IR (film on NaCl, cm^{-1}): 3355*br*, 2953*w*, 2919*w*, 2875*w*, 2853*w*, 1605*s*, 1590*m*, 1547*m*, 1479*m*, 1447*s*, 1317*s*, 1272*w*, 1160*s*, 1070*m*, 1000*w*, 856*w*, 506*s*.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{37}H_{40}N_3O_4$: 590.30133; found: 590.30094. *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{39}N_3NaO_4$: 612.28328; found: 612.28283.

Ru(2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine)Cl$_3$ (7a)



To a mixture of **5c** (0.086 g, 1 eq, 0.15 mmol) in EtOH (20 ml) was added $RuCl_3 \cdot 3H_2O$ (0.038 g, 1 eq, 0.15 mmol). The reaction mixture was heated to 85 °C for 20 h. The solvent was removed in vacuo. The resulting brown solid was suspended in water (70 ml), collected by filtration, washed on the filter with an additional amount of water (until colorless) and acetonitrile (until colorless). The product was dried under vacuum to give the desired compound **7a** (0.109g, 94%) as an insoluble, dark brown solid.

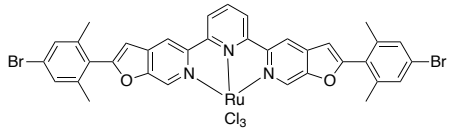
Mp:>300 °C.

IR (KBr, cm^{-1}): 3407*br*, 2967*m*, 2927*m*, 1639*w*, 1607*s*, 1594*s*, 1558*s*, 1458*s*, 1384*s*, 1309*s*, 1277*m*, 1262*m*, 1158*m*, 1078*w*, 1035*m*, 1006*m*, 966*w*, 911*w*, 886*w*, 859*m*, 813*m*, 746*w*, 736*w*, 670*w*, 662*w*, 642*w*, 588*w*, 519*w*, 484*w*.

MS (ESI) m/z: 691.1 ($[M - 2 Cl]^+$).

HRMS (ESI) m/z: $[M - 2 Cl]^+$ calculated for ($C_{35}H_{28}ClN_3O_4Ru$): 691.08121; found: 691.08107.

Ru(2,6-bis(2-(4-bromo-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)pyridine)Cl$_3$ (7b)

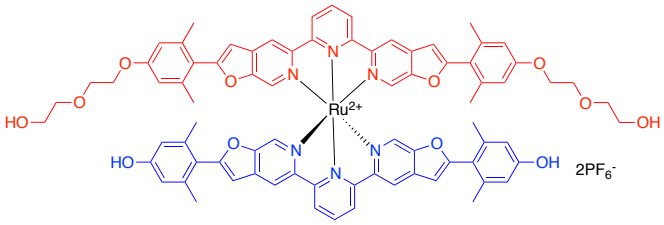


A mixture of 2,6-bis(2-(4-bromo-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)pyridine (**5a**) (150 mg, 1.0 eq, 0.221 mmol) and $RuCl_3 \cdot 3H_2O$ (57.7 mg, 1.0 eq, 0.221 mmol) in ethanol (27 mL) under N_2 atmosphere was heated to reflux for 18 h. The dark brown suspension was allowed to cool to room temperature, and the solvent was evaporated under reduced pressure. The resulting brown solid was suspended in water (50 ml), collected by filtration, washed on the filter with an additional amount of water (until colorless) and acetonitrile (until colorless). The product was dried under vacuum to give the desired compound **7b** (173 mg, 88%) as an insoluble, dark brown solid.

Mp: >350 °C

IR (KBr, cm^{-1}): 3042*w*, 2920*w*, 2851*w*, 1617*m*, 1573*s*, 1456*s*, 1384*m*, 1318*w*, 1245*m*, 1011*m*, 914*m*, 888*w*, 857*m*, 814*w*, 738*w*, 661*w*.

Ru(2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine)⊃(2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)diethanol))$(PF_6)_2$ (8a)



To a mixture of 2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)diethanol (**5d**) (200 mg, 1.0 eq, 0.274 mmol) and Ru(2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)- pyridine)Cl_3 (**7a**) (209 mg, 1.0 eq, 0.274 mmol) in degassed EtOH (100 mL) under N_2 atmosphere was added *N*-ethylmorpholine (0.081 mL, 2.3 eq, 0.636 mmol). The reaction mixture was heated to reflux for 20 h. The mixture was allowed to cool to room temperature and sat. aq. KPF_6 was added. The resulting precipitate was collected by filtration over Celite, washed on the filter with excess water, Et_2O, hexane:EtOAc 1:1 and re-dissolved with acetonitrile into a clean flask. The solvent was evaporated and resulting residue was purified by silica gel column chromatography– first, a brown/green band was eluted by using the 1st eluent (MeCN:H_2O:aq.KPF_6 97:3:0.3), then a red band containing the product **8a** was moved by using 2nd eluent (MeCN:CH_2Cl_2:H_2O:aq.KPF_6 51:9:3:1).

The combined product fractions were evaporated under reduced pressure, re-dissolved in acetonitrile and re-precipitated by addition of sat. aq. KPF_6. The resulting precipitate was collected over Celite, washed on the filter with excess water, Et_2O and re-dissolved into a clean flask. After evaporation of solvent the desired product **8a** (288 mg, 63%) was obtained as a red solid.

Mp: >200 °C dec.

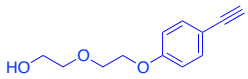
^{1}H NMR (500 MHz, CD_3CN, δ): 8.82 (s, 2H), 8.82 (s, 2H), 8.75 (d, *J* = 8.2 Hz, 2H), 8.75 (d, *J* = 8.1 Hz, 2H), 8.43 (t, *J* = 8.2 Hz, 1H), 8.43 (t, *J* = 8.1 Hz, 1H), 7.69 (s, 2H), 7.68 (s, 2H), 7.16 (s, 2H), 6.97 (s, 2H), 6.94 (s, 2H), 6.70 (s, 4H), 6.56 (s, 4H), 4.15-4.06 (m, 4H), 3.79-3.74 (m, 4H), 3.64-3.57 (m, 4H), 3.57-3.49 (m, 4H), 2.83 (t, *J* = 5.4 Hz, 2H), 2.03 (s, 12H), 1.99 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 163.2, 162.9, 161.0, 159.4, 156.9, 153.0, 153.0, 152.6, 152.6, 141.3, 141.3, 137.5, 137.5, 137.3, 137.3, 136.7, 123.1, 123.1, 121.8, 120.8, 117.8, 117.8, 115.6, 114.8, 107.9, 107.8, 73.3, 70.1, 68.5, 61.9, 20.7, 20.6.

IR (KBr, cm^{-1}): 3431*br*, 3125*w*, 2953*w*, 2921*w*, 2871*w*, 1607*m*, 1454*s*, 1384*w*, 1313*m*, 1288*w*, 1276*w*, 1158*m*, 1128*w*, 1065*w*, 1031*w*, 1005*w*, 843*s*, 739*w*, 558*m*.

HRMS (ESI) *m/z*: $[M\text{-}2PF_6]^{2+}$ calcd for $C_{78}H_{70}N_6O_{12}Ru$: 692.20529; found: 692.20595.

2-(2-(4-ethynylphenoxy)ethoxy)ethanol



To a mixture of 2-(2-(4-iodophenoxy)ethoxy)ethanol (prepared according to the literature procedures[5]) (2.5 g, 1.0 eq, 8.11 mmol), $Pd(PPh_3)_2Cl_2$ (171 mg, 3 mol%, 0.243 mmol) and CuI (46 mg, 3 mol%, 0.243 mmol) in triethylamine (30 mL) under N_2 atmosphere was added trimethylsilylacetylene (2.3 mL, 2.0 eq, 16 mmol). The reaction mixture was heated to 75 °C for 18 h. The mixture was allowed to cool to room temperature, and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in minimum amount of CH_2Cl_2 and filtered through a plug of silica gel eluting with EtOAc. The filtrate was evaporated under reduced pressure to give crude 2-(2-(4-((trimethylsilyl)ethynyl)phenoxy)ethoxy)ethanol.

^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.39 (AA′BB′ spin system, 2H), 8.83 (AA′BB′ spin system, 2H), 4.16-4.08 (m, 2H), 3.89-3.82 (m, 2H), 3.78-3.72 (m, 2H), 3.70-3.62 (m, 2H), 0.23 (s, 9H).

The obtained product was dissolved in a mixture of MeOH (32 mL) and CH_2Cl_2 (5 mL). To the solution KF (4.7 g, 10 eq, 81 mmol) was added and the mixture was heated to 50 °C for 4 h. The solvent was evaporated under reduced pressure and the resulting residue was filtered through a plug of silica gel eluting with CH_2Cl_2. The solvent from the filtrate was evaporated under reduced pressure to give desired 2-(2-(4-ethynylphenoxy)ethoxy)ethanol (1.65 g, 99% over 2 steps) as a yellowish oil.

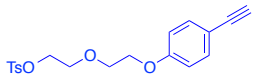
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.42 (AA′BB′ spin system, 2H), 6.86 (AA′BB′ spin system, 2H), 4.15-4.13 (m, 2H), 3.87-3.85 (m, 2H), 3.77-3.75 (m, 2H), 3.68-3.66 (m, 2H), 3.00 (s, 1H), 2.09 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.2, 133.7, 114.7, 114.7, 83.7, 76.1, 72.7, 69.7, 67.6, 61.9.

IR (film on NaCl, cm^{-1}): 3418*br*, 3285*s*, 3043*w*, 2931*s*, 2877*s*, 2537*w*, 2105*m*, 1605*s*, 1572*m*, 1505*s*, 1455*s*, 1356*m*, 1289*s*, 1250*s*, 1173*s*, 1131*s*, 1059*s*, 929*m*, 888*m*, 837*m*, 538*w*.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{14}NaO_3$: 229.08352; found: 229.08328.

2-(2-(4-ethynylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate (11)



To a solution of 2-(2-(4-ethynylphenoxy)ethoxy)ethanol (1.49 g, 1.0 eq, 7.22 mmol), DMAP (26 mg, 0.3 eq, 0.22 mmol) and triethylamine (3.0 mL, 3.0 eq, 21 mmol) in CH_2Cl_2 (50 mL) was added 4-toluenesulfonyl chloride (2.20 g, 1.5 eq, 11.6 mmol) in one portion. The reaction mixture was stirred for 2.5 h at room temperature. The reaction was quenched with water (100 ml), the organic layer was separated, washed with water (2 × 50 ml), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (eluent hexane:EtOAc 3:1) to give 2-(2-(4-ethynylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**11**) (1.99 g, 76%) as a yellowish oil.

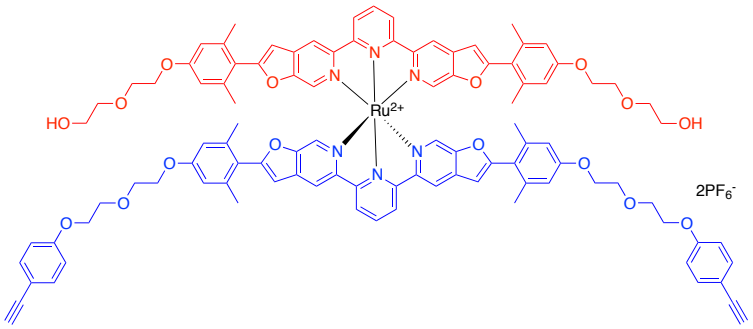
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.79 (AA′BB′ spin system, 2H), 7.41 (AA′BB′ spin system, 2H), 7.30 (AA′BB′ spin system, 2H), 6.82 (AA′BB′ spin system, 2H), 4.20-4.18 (m. 2H), 4.05-4.04 (m, 2H), 3.79-3.77 (m, 2H), 3.76-3.74 (m, 2H), 3.00 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.1, 145.0, 133.7, 133.1, 129.9, 128.1, 125.5, 114.7, 83.7, 76.1, 69.9, 69.3, 69.1, 67.6, 21.8.

IR (film on NaCl, cm^{-1}): 3281*m*, 3065*w*, 3045*w*, 2922*w*, 2877*w*, 2105*w*, 1605*m*, 1572*w*, 1506*s*, 1454*w*, 1399*w*, 1355*s*, 1289*m*, 1249*m*, 1189*m*, 1176*s*, 1138*m*, 1018*w*, 919*m*, 836*m*, 815*m*, 775*w*, 663*m*, 554*w*.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{20}NaO_5S$: 383.09237; found: 383.09267.

Ru(2,6-bis(2-(4-(2-(2-(4-ethynylphenoxy)ethoxy)ethoxy)-2,6-dimethylphenyl)furo[2,3-*c*]pyridin-5-yl)pyridine)⊃(2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)diethanol))$(PF_6)_2$ (8b)



To a mixture of heteroleptic Ru(II) complex **8a** (200 mg, 1.0 eq, 0.119 mmol), 2-(2-(4-ethynylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**11**) (94.7 mg, 2.2 eq, 0.263 mmol) and anhydrous Cs_2CO_3 (117 mg, 3.0 eq, 0.358 mmol) under N_2 atmosphere was added anhydrous DMF (37 mL). The reaction mixture was heated to 80 °C for 9.5 h, allowed to cool to room temperature and sat. aq. KPF_6 was added. The resulting red precipitate was collected by filtration over Celite, washed on the filter with excess water, Et_2O, hexane:EtOAc 3:1 and re-dissolved into a clean flask. After evaporation of solvent and drying under vacuum the desired complex **8b** was obtained as a red solid (226 mg, 92%).

Mp: >247 °C dec.

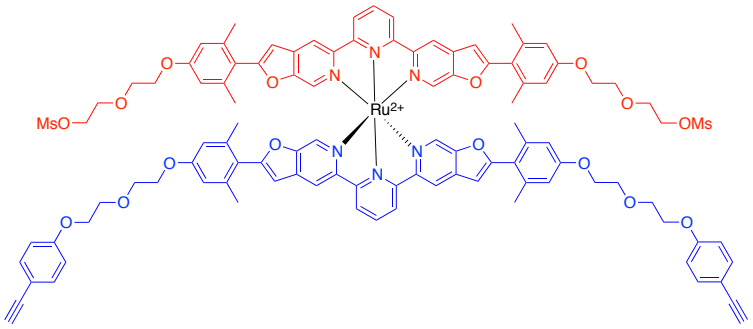
^{1}H NMR (500 MHz, CD_3CN, δ): 8.82 (s, 4H), 8.74 (d, *J* = 8.2 Hz, 4H), 8.43 (t, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 0.9 Hz, 4H), 7.39 (AA′BB′ spin system, 4H), 6.98 (d, *J* = 0.9 Hz, 2H), 6.97 (d, *J* = 0.9 Hz, 2H), 6.88 (AA′BB′ spin system, 4H), 6.71 (s, 4H), 6.68 (s, 4H), 4.13-4.09 (m, 12H), 3.86-3.79 (m, 8H), 3.79-3.73 (m, 4H), 3.61-3.58 (m, 4H), 3.56-3.51 (m, 4H), 3.25 (s, 2H), 2.67 (t, *J* = 5.6 Hz, 2H), 2.04 (s, 12H), 2.03 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 163.0, 161.1, 161.1, 160.3, 156.9, 153.0, 152.6, 141.3, 141.2, 137.4, 137.3, 136.7, 134.5, 123.1, 121.6, 117.8, 115.7, 115.1, 114.8, 114.8, 107.8, 84.2, 77.5, 73.5, 70.3, 70.3, 70.1, 68.6, 68.5, 68.4, 62.0, 20.7.

IR (film on NaCl, cm^{-1}): 3744*w*, 3310*w*, 3282*w*, 2953*w*, 2919*w*, 2871*w*, 2103*w*, 1604*s*, 1506*m*, 1384*w*, 1313*m*, 1289*m*, 1250*m*, 1162*m*, 1130*m*, 1067*w*, 1031*w*, 1004*w*, 841*s*, 808*w*, 735*w*, 558*m*.

HRMS (ESI) *m/z*: $[M\text{-}2PF_6]^{2+}$ calcd for $C_{102}H_{94}N_6O_{16}Ru$: 880.28820; found: 880.28864.

Ru(2,6-bis(2-(4-(2-(2-(4-ethynylphenoxy)ethoxy)ethoxy)-2,6-dimethylphenyl)furo[2,3-*c*]pyridin-5-yl)pyridine)⊃(2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)bis(ethane-2,1-diyl) dimethanesulfonate)$(PF_6)_2$ (8c)



To a solution of heteroleptic Ru(II) complex **8b** (40.0 mg, 1.0 eq, 0.0195 mmol) in a mixture of anhydrous THF (3 mL) and acetonitrile (0.5 mL) under Ar atmosphere was added triethylamine (163 μL, 60 eq, 1.17 mmol) and methanesulfonyl chloride (45 μL, 30 eq, 0.58 mmol) that caused formation of precipitate. The reaction mixture was stirred for 2 h at room temperature. To the mixture sat. aq. KPF_6 was added, and the resulting red precipitate was collected by filtration over Celite, washed with excess water, Et_2O, hexane:Et_2O 1:1 and re-dissolved into a clean flask. After evaporation of solvent and drying under vacuum the desired product **8c** (39.4 mg, 92%) was obtained as a red solid.

Mp: >239 °C dec.

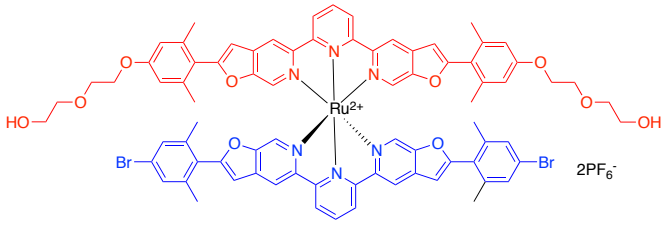
^1H NMR (400 MHz, CD_3CN, δ): 8.82 (s, 4H), 8.74 (d, J = 8.2 Hz, 4H), 8.43 (t, J = 8.1 Hz, 2H), 7.69 (s, 2H), 7.69 (s, 2H), 7.39 (AA′BB′ spin system, 4H), 6.98 (d, J = 0.9 Hz, 2H), 6.97 (d, J = 0.9 Hz, 2H), 6.88 (AA′BB′ spin system, 4H), 6.70 (s, 4H), 6.68 (s, 4H), 4.35-4.28 (m, 4H), 4.14-4.09 (m, 12H), 3.87-3.76 (m, 12H), 3.79-3.71 (m, 4H), 3.25 (s, 2H), 3.02 (s, 6H), 2.04 (s, 12H), 2.03 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 163.0, 163.0, 161.1, 161.0, 160.3, 156.9, 153.0, 152.6, 141.3, 141.2, 137.4, 137.3, 136.7, 134.5, 123.1, 121.7, 121.6, 117.8, 115.7, 115.1, 114.8, 114.8, 107.8, 84.2, 77.5, 70.9, 70.3, 70.3, 70.3, 69.8, 68.6, 68.4, 68.3, 37.7, 20.7.

IR (film on NaCl, cm^{-1}): 3310*w*, 3281*w*, 3125*w*, 3043*w*, 2957*w*, 2919*w*, 2875*w*, 2103*w*, 1604*m*, 1508*m*, 1455*s*, 1351*m*, 1313*s*, 1289*m*, 1251*m*, 1163*m*, 1133*m*, 1071*w*, 1005*w*, 974*w*, 923*w*, 914*w*, 841*s*, 807*w*, 735*w*, 558*w*.

HRMS (ESI) *m/z*: $[M-2PF_6]^{2+}$ calcd for $C_{104}H_{98}N_6O_{20}RuS_2$: 958.26572; found: 958.26570.

Ru(2,6-bis(2-(4-bromo-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)pyridine)⊃(2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)diethanol))$(PF_6)_2$ (9a)



A mixture of Ru(2,6-bis(2-(4-bromo-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)pyridine)Cl_3 (**7b**) (134 mg, 1.0 eq, 0.151 mmol), 2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)diethanol (**5d**) (110 mg, 1.0 eq, 0.151 mmol) and *N*-ethylmorpholine (44.6 μL, 2.3 eq, 0.350 mmol) in EtOH (36 mL) was heated to reflux for 24 h. The reaction mixture was allowed to cool down to room temperature and sat. aq. KPF_6 was added. The resulting brown precipitate was filtered over Celite, washed on the filter with excess water, EtOAc, Et_2O and re-dissolved with acetonitrile into a clean flask. After evaporation of solvent the resulting brown solid was purified by silica gel column chromatography – first, a brown band was eluted by using the 1st eluent (MeCN:H_2O:aq.KPF_6 97:3:0.3), then a red band containing the desired product **9a** was moved by using the 2nd eluent (MeCN:H_2O:aq.KPF_6 95:5:1). The combined product fractions were evaporated under reduced pressure, re-dissolved in acetonitrile and sat. aq. KPF_6 was added. The resulting precipitate was collected by filtration over Celite, washed with excess water,

Et_2O and re-dissolved with acetonitrile into a clean flask. After evaporation the desired product **9a** (114 mg, 42%) was obtained as a red solid. Recrystallization by slow Et_2O vapor diffusion into the acetone solution of **9a** gave single crystals suitable for X-ray diffraction analysis.

Mp: >320 °C dec.

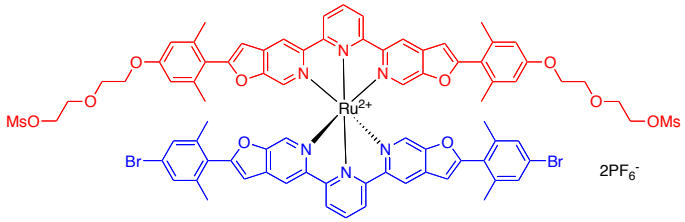
^{1}H NMR (400 MHz, CD_3CN, δ): 8.85 (d, *J* = 0.8 Hz, 2H), 8.82 (d, *J* = 0.8 Hz, 2H), 8.75 (d, *J* = 8.2 Hz, 2H), 8.75 (d, *J* = 8.2 Hz, 2H), 8.43 (t, *J* = 8.1 Hz, 1H), 8.43 (t, *J* = 8.1 Hz, 1H), 7.72 (s, 2H), 7.69 (s, 2H), 7.35 (s, 4H), 7.05 (d, *J* = 0.8 Hz, 2H), 6.98 (d, *J* = 0.8 Hz, 2H), 6.71 (s, 4H), 4.14-4.06 (m, 4H), 3.84-3.73 (m, 4H), 3.65-3.57 (m, 4H), 3.56-3.50 (m, 4H), 2.69 (br. s, 2H), 2.04 (s, 12H), 2.04 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 163.0, 161.3, 161.1, 156.9, 156.8, 153.1, 152.9, 152.7, 152.5, 141.8, 141.3, 137.7, 137.5, 137.3, 137.2, 136.8, 136.8, 131.6, 128.4, 125.0, 123.2, 123.1, 121.6, 117.8, 114.8, 108.4, 107.8, 73.5, 70.1, 68.5, 62.0, 20.7, 20.3.

IR (film on NaCl, cm^{-1}): 3427*s*, 2925*w*, 2866*w*, 1603*m*, 1454*s*, 1384*w*, 1313*m*, 1251*w*, 1162*w*, 1127*w*, 1068*w*, 1007*w*, 842*vs*, 558*m*.

HRMS (ESI) *m/z*: $[M\text{-}2PF_6]^{2+}$ calcd for $C_{78}H_{68}Br_2N_6O_{10}Ru$: 755.12012; found: 755.12074.

Ru(2,6-bis(2-(4-bromo-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)pyridine) ⊃(2,2′-(2,2′-(4,4′-(5,5′-(pyridine-2,6-diyl)bis(furo[2,3-*c*]pyridine-5,2-diyl))bis(3,5-dimethyl-4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)bis(ethane-2,1-diyl) dimethanesulfonate)(PF_6)$_2$ (9b)



To a solution of **9a** (44.2 mg, 1.0 eq, 0.0246 mmol) in a mixture of anhydrous THF (3.5 mL) and acetonitrile (1.5 mL) under Ar atmosphere were added triethylamine (0.137 mL, 40 eq, 0.982 mmol) and methanesulfonyl chloride (0.048 mL, 20 eq, 0.491 mmol). The reaction mixture was stirred for 1 h at room temperature. To the mixture was added sat. aq. KPF_6 to cause precipitation. The resulting red solid was collected by filtration over Celite, washed on the filter with excess water, Et_2O and

1:1 hexane:EtOAc then re-dissolved with acetonitrile into a clean flask. After evaporation of solvent and drying under vacuum the desired product **9b** (47.5 mg, 99%) was obtained as a red solid.

Mp: >230 °C.

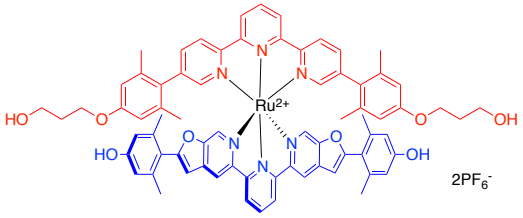
^{1}H NMR (400 MHz, CD_3CN, δ): 8.85 (d, *J* = 0.8 Hz, 2H), 8.82 (d, *J* = 0.8 Hz, 2H), 8.75 (d, *J* = 8.2 Hz, 2H), 8.74 (d, *J* = 8.2 Hz, 2H), 8.44 (t, *J* = 8.2 Hz, 1H), 8.43 (t, *J* = 8.2 Hz, 1H), 7.72 (s, 2H), 7.69 (s, 2H), 7.35 (s, 4H), 7.05 (d, *J* = 0.8 Hz, 2H), 6.98 (d, *J* = 0.8 Hz, 2H), 6.70 (s, 4H), 4.35-4.28 (m, 4H), 4.15-4.07 (m, 4H), 3.83-3.76 (m, 4H), 3.79-3.72 (m, 4H), 3.02 (s, 6H), 2.04 (s, 12H), 2.04 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 162.0, 160.3, 160.0, 155.9, 155.9, 152.1, 151.9, 151.7, 151.6, 140.8, 140.3, 136.7, 136.5, 136.3, 136.2, 135.8, 135.8, 130.6, 127.4, 124.1, 122.2, 122.1, 120.7, 116.8, 113.8, 107.4, 106.8, 69.9, 69.3, 68.8, 67.3, 36.7, 19.7, 19.3.

IR (film on NaCl, cm^{-1}): 2957*w*, 2925*w*, 2858*w*, 1603*m*, 1455*s*, 1351*w*, 1313*m*, 1251*w*, 1175*m*, 1164*m*, 1072*w*, 1008*w*, 840*vs*, 558*m*.

HRMS (ESI) *m/z*: $[M\text{-}2PF_6]^{2+}$ calcd for $C_{80}H_{72}Br_2N_6O_{14}RuS_2$: 833.09763; found: 833.09738.

Ru(2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine)⊃(3,3′-(((2,2′:6′,2″-terpyridine)-5,5″-diylbis(3,5-dimethyl-4,1-phenylene))bis(oxy))bis(propan-1-ol))(PF_6)$_2$ (10a)



To a mixture of 3,3′-(((2,2′:6′,2″-terpyridine)-5,5″-diylbis(3,5-dimethyl-4,1-phenylene))bis(oxy))bis(propan-1-ol) (**6c**) (220mg, 1.1 eq, 0.374 mmol) and Ru(2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine)Cl_3 (**7a**) (260 mg, 1.0 eq, 0.341 mmol) in degassed EtOH (100 mL) under N_2 atmosphere was added *N*-ethylmorpholine (0.11 mL, 2.3 eq, 0.86 mmol). The reaction mixture was heated to reflux for 24 h. The mixture was allowed to cool to room temperature and sat. aq. KPF_6 was added. The resulting precipitate was collected by filtration over Celite, washed on the filter with excess water, Et_2O, hexane:EtOAc 1:1 and re-dissolved with

acetonitrile into a clean flask. The solvent was evaporated and the resulting residue was purified by silica gel column chromatography – first, a brown/green band was eluted by using the 1st eluent (MeCN:H_2O:aq.KPF_6 97:3:0.3), then a red band containing the product **10a** was moved by the 2nd eluent (MeCN:CH_2Cl_2:H_2O:aq.KPF_6 90:15:4:1). The combined product fractions were evaporated under reduced pressure, re-dissolved in acetonitrile and re-precipitated by addition of sat. aq. KPF_6. The resulting precipitate was collected over Celite, washed on the filter with excess water, Et_2O and re-dissolved with acetonitrile into a clean flask. After evaporation of solvent the desired product **10a** (244 mg, 47%) was obtained as a red solid.

Mp: >300 °C dec.

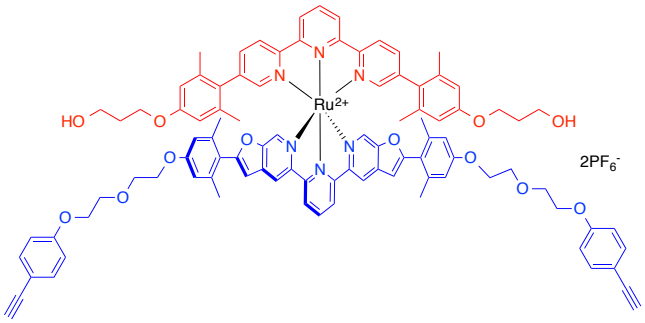
^{1}H NMR (500 MHz, CD_3CN, δ): 8.83 (dd, *J* = 8.2, 2.1 Hz, 2H), 8.78 (d, *J* = 2.4 Hz, 2H), 8.62 (dd, *J* = 8.3, 2.3 Hz, 2H), 8.57 (dd, *J* = 8.5, 1.8 Hz, 2H), 8.46 (td, *J* = 8.2, 1.6 Hz, 1H), 8.27 (t, *J* = 8.1 Hz, 1H), 7.73 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.69 (d, *J* = 3.3 Hz, 2H), 7.33 (s, 2H), 7.18 (s, 2H), 6.99 (s, 2H), 6.57 (s, 4H), 6.54 (s, 4H), 3.97 (t, *J* = 6.3 Hz, 4H), 3.62 (t, *J* = 6.2 Hz, 4H), 2.75 (s, 2H), 2.03 (s, 12H), 1.86 (p, *J* = 6.3 Hz, 4H), 1.48 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 163.4, 159.8, 159.3, 157.6, 156.7, 156.3, 153.4, 152.7, 152.1, 141.3, 141.1, 140.2, 138.2, 137.5, 137.4, 137.0, 136.6, 128.3, 124.9, 124.5, 123.0, 120.6, 117.7, 115.5, 114.5, 107.7, 65.6, 59.1, 32.9, 20.6, 20.5.

IR (film on NaCl, cm^{-1}): 3513*br*, 3448*br*, 3116*w*, 2957*w*, 2922*w*, 2875*w*, 1604*m*, 1456*s*, 1312*m*, 1276*m*, 1157*m*, 1067*w*, 1030*w*, 1009*w*, 841*vs*, 807*m*, 555*m*.

HRMS (ESI) *m/z*: $[M\text{-}2PF_6]^{2+}$ calcd for $C_{72}H_{66}N_6O_8Ru$: 622.19873; found: 622.20047.

Ru(2,6-bis(2-(4-(2-(2-(4-ethynylphenoxy)ethoxy)ethoxy)-2,6-dimethylphenyl)furo[2,3-*c*]pyridin-5-yl)pyridine)⊃(3,3′-(((2,2′:6′,2″-terpyridine)-5,5″-diylbis(3,5-dimethyl-4,1-phenylene))bis(oxy))bis(propan-1-ol))$(PF_6)_2$ (10b)



To a mixture of heteroleptic Ru(II) complex **10a** (50.0 mg, 1.0 eq, 0.0326 mmol), 2-(2-(4-ethynylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**11**) (30.0 mg, 2.55 eq, 0.0831 mmol) and anhydrous Cs_2CO_3 (31.5 mg, 3.0 eq, 0.0968 mmol) under N_2 atmosphere was added anhydrous DMF (9 mL). The reaction mixture was heated to 75 °C for 5 h, allowed to cool to room temperature and sat. aq. KPF_6 was added. The resulting red precipitate was collected by filtration over Celite, washed on the filter with excess water, Et_2O, hexane:EtOAc 3:1 and re-dissolved into a clean flask. The solvent was evaporated and the resulting residue was purified by silica gel column chromatography – first, the fast moving bands were eluted by using the 1st eluent (MeCN:H_2O:aq.KPF_6 97:3:0.3), then a bright red band containing the product **10b** was moved by the 2nd eluent (MeCN:CH_2Cl_2:H_2O:aq.KPF_6 97:17:3:0.3). The combined product fractions were evaporated, dissolved in CH_2Cl_2, filtered through a frit filter and evaporated to give the desired product **10b** (25 mg, 40%).

Mp: >210 °C dec.

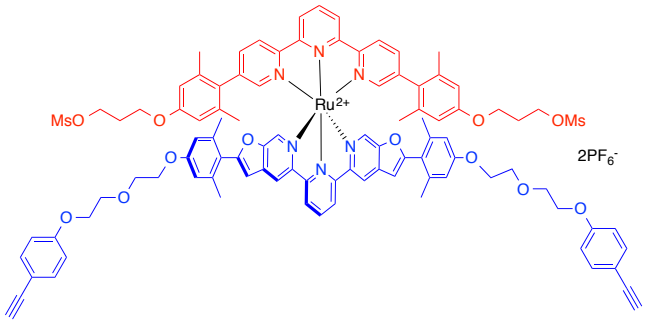
^{1}H NMR (500 MHz, CD_3CN, δ): 8.80 (dd, *J* = 8.2, 1.5 Hz, 2H), 8.76 (s, 2H), 8.60 (dd, *J* = 8.2, 1.5 Hz, 2H), 8.55 (d, *J* = 8.3 Hz, 2H), 8.44 (td, *J* = 8.1, 1.5 Hz, 1H), 8.26 (td, *J* = 8.2, 1.4 Hz, 1H), 7.73 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.66 (s, 2H), 7.40 (AA′BB′ spin system, 4H), 7.15 (s, 2H), 6.99 (s, 2H), 6.88 (AA′BB′ spin system, 4H), 6.70 (s, 4H), 6.55 (s, 4H), 4.16–4.07 (m, 8H), 3.98 (td, *J* = 6.3, 1.5 Hz, 4H), 3.85–3.79 (m, 8H), 3.61 (t, *J* = 6.3 Hz, 4H), 3.26 (s, 2H), 2.64 (s, 2H), 2.06 (s, 12H), 1.87 (p, *J* = 6.2 Hz, 4H), 1.47 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 163.2, 161.1, 160.3, 159.9, 157.6, 156.7, 156.3, 153.4, 152.8, 152.1, 141.2, 141.2, 140.3, 138.3, 137.5, 137.5, 137.0, 136.6, 134.4, 128.3, 125.0, 124.5, 123.0, 121.5, 117.8, 115.7, 115.0, 114.8, 114.5, 107.8, 84.2, 77.5, 70.3, 70.3, 68.6, 68.4, 65.6, 59.1, 33.0, 20.7, 20.5.

IR (film on NaCl, cm^{-1}): 3748*w*, 3283*w*, 3310*w*, 2953*w*, 2918*w*, 2879*w*, 2853*w*, 2103*w*, 1603*s*, 1505*m*, 1455*s*, 1314*m*, 1279*m*, 1250*m*, 1162*m*, 1069*w*, 1030*w*, 841*vs*, 809*w*, 733*w*, 701*w*, 663*w*, 558*w*.

HRMS (ESI) *m/z*: $[M\text{-}2PF_6]^{2+}$ calcd for $C_{96}H_{90}N_6O_{12}Ru$: 810.28246; found: 810.28334.

Ru(2,6-bis(2-(4-(2-(2-(4-ethynylphenoxy)ethoxy)ethoxy)-2,6-dimethylphenyl)furo[2,3-*c*]pyridin-5-yl)pyridine)⊃(((2,2′:6′,2″-terpyridine)-5,5″-diylbis(3,5-dimethyl-4,1-phenylene))bis(oxy))bis(propane-3,1-diyl) dimethanesulfonate)$(PF_6)_2$ (10c)



To a solution of heteroleptic Ru(II) complex **10b** (23.6 mg, 1.0 eq, 0.01235 mmol) in a mixture of anhydrous THF (2 mL) and MeCN (0.3 mL) under Ar atmosphere was added triethylamine (120 µL, 70 eq, 0.860 mmol) and methanesulfonyl chloride (34 µL, 36 eq, 0.44 mmol) that caused formation of precipitate. The reaction mixture was stirred for 1.5 h at room temperature. To the mixture sat. aq. KPF_6 was added, and the resulting red precipitate was collected by filtration over Celite, washed with excess water, Et_2O, hexane:Et_2O 1:1 and re-dissolved with acetonitrile into a clean flask. After evaporation of solvent and drying under vacuum the desired product **10c** (24.7 mg, 97%) was obtained as a red solid.

Mp: >200 °C dec.

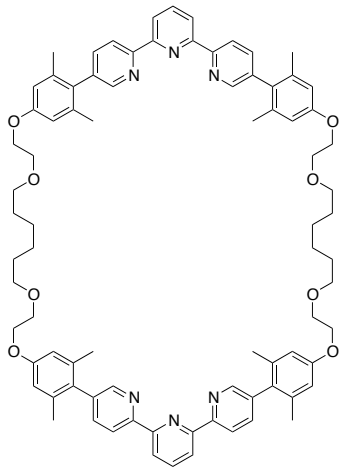
^1H NMR (500 MHz, CD_3CN, δ): 8.80 (d, *J* = 8.1 Hz, 2H), 8.76 (s, 2H), 8.60 (d, *J* = 8.1 Hz, 2H), 8.55 (d, *J* = 8.2 Hz, 2H), 8.44 (t, *J* = 8.1 Hz, 1H), 8.27 (t, *J* = 8.1 Hz, 1H), 7.73 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.66 (s, 2H), 7.40 (AA′BB′ spin system, 4H), 7.16 (s, 2H), 7.00 (s, 2H), 6.88 (AA′BB′ spin system, 4H), 6.71 (s, 4H), 6.56 (s, 4H), 4.34 (t, *J* = 6.1 Hz, 4H), 4.15–4.10 (m, 8H), 4.00 (t, *J* = 6.0 Hz, 4H), 3.88–3.79 (m, 8H), 3.26 (s, 2H), 3.00 (s, 6H), 2.12 (p, *J* = 6.4, 6.0 Hz, 4H), 2.06 (s, 12H), 1.48 (s, 12H).

^{13}C NMR (125 MHz, CD_3CN, δ): 163.2, 161.1, 160.3, 159.5, 157.6, 156.8, 156.3, 153.4, 152.8, 152.2, 141.2, 141.1, 140.3, 138.4, 137.5, 137.5, 137.0, 136.6, 134.5, 128.7, 125.0, 124.5, 123.0, 121.5, 117.8, 115.7, 115.1, 114.8, 114.6, 107.8, 84.2, 77.5, 70.3, 70.3, 68.6, 68.4, 68.4, 64.4, 37.3, 29.7, 20.7, 20.5.

IR (film on NaCl, cm^{-1}): 3310*w*, 3280*w*, 2953*w*, 2918*w*, 2879*w*, 2849*w*, 2108*w*, 1604*s*, 1506*m*, 1455*s*, 1352*m*, 1314*m*, 1279*w*, 1250*m*, 1172*m*, 1163*s*, 1134*w*, 1068*w*, 947*w*, 841*vs*, 809*w*, 734*w*, 559*w*.

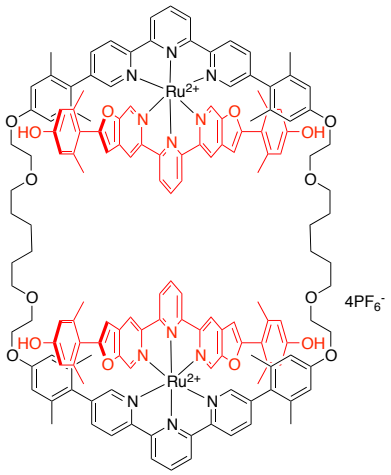
HRMS (ESI) *m/z*: $[M-2PF_6]^{2+}$ calcd for $C_{98}H_{94}N_6O_{16}RuS_2$: 888.26001; found: 888.26039.

bis-(5'5''-bis-(4-(2-propoxyethoxy)-2,6-dimethylphenyl)-2,2':6',2''-terpyridine) macrocycle 12



Macrocycle **12** was synthesized according to the previousely reported procedure[6].

bis-(5′,5″-bis-(4-(2-propoxyethoxy)-2,6-dimethylphenyl)-2,2′:6′,2″-terpyridine) macrocycle⊃bis-(Ru(2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine))$(PF_6)_4$ (13)



In dry 25 ml two-necked flask equipped with magnetic stirring bar, reflux condenser and septum a solid mixture of macrocycle **12**[6] (66.9 mg, 1.0 eq, 0.0520 mmol) and Ru(2,6-bis-(2-(4-hydroxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-pyridine)Cl_3 (119 mg, 3.0 eq, 0.156 mmol) (**7a**) was 3 × degassed and refilled with Ar. To the degassed mixture EtOH (22 mL) was added through the septum. The reaction mixture was brought to reflux and *N*-ethylmorpholine (~10 μL, 1.6 eq, 0.082 mmol) was added through the septum. The reaction mixture was heated to reflux for 24 h and allowed to cool to room temperature. To the mixture sat. aq. KPF_6 (60 ml) was added. The resulting brown precipitate was filtered over Celite, washed on the filter with excess water and Et_2O, and then re-dissolved with acetone into a clean flask (green solid remains on Celite). The obtained red solution was evaporated under reduced pressure to give a brown residue that was purified by silica gel column chromatography – first, a brown/green band was eluted by using the 1st eluent (MeCN:CH_2Cl_2:H_2O:aq.KPF_6 320:100:10:1), then a red band containing the desired product **13** was moved by the 2nd eluent (MeCN:CH_2Cl_2:H_2O:aq.KPF_6 345:90:15:4). The product fractions were evaporated, re-dissolved in acetone, and to the solution sat. aq. KPF_6 was added. The resulting precipitate was collected by filtration over Celite, washed with excess water, Et_2O and re-dissolved with acetone into a clean flask. After evaporation of solvent and drying under vacuum the desired product **13** (50.8 mg, 31%) was obtained as a red solid.

X-ray quality crystals were grown by slow vapour diffusion of Et_2O into a MeCN solution of **13**.

Mp: >295 °C dec.

^{1}H NMR (500 MHz, Acetone-d_6, δ): 9.13 (d, J = 8.0 Hz, 4H), 9.12 (s, 4H), 8.88 (d, J = 8.3 Hz, 4H), 8.87 (d, J = 8.4 Hz, 4H), 8.62 (t, J = 8.2 Hz, 2H), 8.37 (t, J =8.2 Hz,

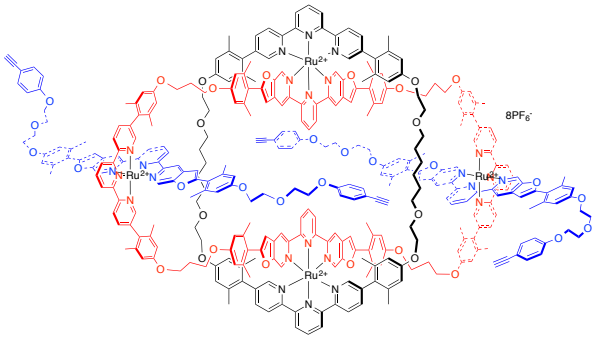
2H), 8.10 (s, 4H), 7.90 (dd, J = 8.3, 1.9 Hz, 4H), 7.56 (d, J = 1.4 Hz, 4H), 7.12 (s, 4H), 6.62 (s, 8H), 6.58 (s, 8H), 4.07 (t, J = 4.6 Hz, 8H), 3.70 (t, J = 4.4 Hz, 8H), 3.48 (t, J = 6.5 Hz, 8H), 2.01 (s, 24H), 1.58-1.52 (m, 8H), 1.50 (s, 24H), 1.40-1.35 (m, 8H).

^{13}C NMR (125 MHz, Acetone-d_6, δ): 163.7, 160.0, 159.8, 157.9, 156.9, 156.5, 153.5, 152.7, 152.5, 141.1, 140.8, 140.3, 137.9, 137.8, 137.3, 137.2, 136.8, 128.3, 125.1, 124.6, 122.9, 120.0, 117.8, 115.7, 114.6, 107.8, 71.7, 69.8, 68.2, 30.5, 26.7, 20.6, 20.4.

IR (neat, cm^{-1}): 3524*w*, 2929*w*, 2865*w*, 1705*w*, 1605*w*, 1454*m*, 1361*w*, 1313*m*, 1277*w*, 1158*w*, 1075*w*, 1031*w*, 1007*w*, 840*s*, 739*w*, 558*m*.

HRMS (ESI) m/z: $[M-4PF_6]^{4+}$ calcd for $C_{152}H_{144}N_{12}O_{16}Ru_2$: 649.22362; found: 649.22274.

Synthesis of the Threaded Ring-in-Ring Complex (1a)



A mixture of threaded macrocycle **13** (9.47 mg, 1.0 eq, 0.00298 mmol), mesylate Ru(II) cap **10c** (13.9 mg, 2.23 eq, 0.00665 mmol), anhydrous K_2CO_3 (11.4 mg, 28 eq, 0.0823 mmol) and activated 4 Å molecular sieve powder (~33 mg) in anhydrous DMF (33 mL) under Ar atmosphere was heated by gradually increasing reaction temperature from 70 to 80 °C over 43 h (The reaction progress was monitored by on-flow ESI-MS. It is extremely important to increase reaction temperature slowly, because there is no reactivity under 70 °C; however, heating up too quickly to 80 °C facilitates polymerization/decomposition). The reaction mixture was allowed to cool to room temperature, and sat. aq. KPF_6 was added. The resulting precipitate was collected by filtration over Celite, washed on the filter with excess water, Et_2O, hexane:EtOAc 3:1 and re-dissolved with acetonitrile into a clean flask. After evaporation of solvent the red residue was purified by silica gel column chromatography (MeCN:CH_2Cl_2:H_2O:aq.KPF_6 97:100:3:0.3). After several fast moving bands, a slow moving red band containing the desired product was collected (fractions controlled by on-flow ESI-MS). The combined product fractions were

evaporated, dissolved in CH_2Cl_2, filtered through a frit filter and evaporated to give the desired product **1a** (4.81 mg, 23 %) as a red solid.

Mp: >255 °C dec.

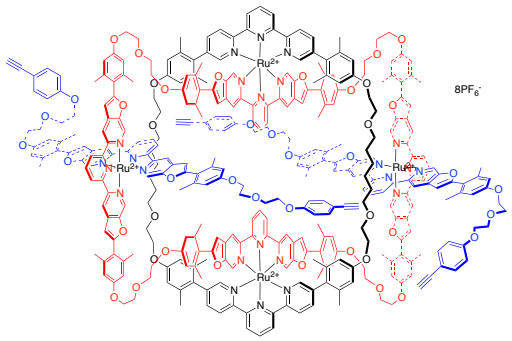
^{1}H NMR (600 MHz, CD_3CN, δ): 8.85 (d, *J* = 8.1 Hz, 4H), 8.84 (s, 4H), 8.80 (d, *J* = 8.3 Hz, 4H), 8.72 (s, 4H), 8.60 (d, *J* = 8.3 Hz, 4H), 8.57 (d, *J* = 8.3 Hz, 4H), 8.55 (d, *J* = 8.3 Hz, 4H), 8.54 (d, *J* = 8.1 Hz, 4H), 8.48 (t, *J* = 8.3 Hz, 2H), 8.43 (t, *J* = 8.3 Hz, 2H), 8.20 (t, *J* = 8.3 Hz, 2H), 8.06 (t, *J* = 8.1 Hz, 2H), 7.76 (dd, *J* = 8.5, 1.9 Hz, 4H), 7.72 (s, 4H), 7.72 (dd, *J* = 8.5, 1.9 Hz, 4H), 7.64 (s, 4H), 7.39 (AA′BB′ spin system, 8H), 7.21 (d, *J* = 1.8 Hz, 4H), 7.11 (d, *J* = 1.9 Hz, 4H), 7.05 (s, 4H), 6.97 (d, *J* = 0.7 Hz, 4H), 6.87 (AA′BB′ spin system, 8H), 6.73 (s, 8H), 6.68 (s, 8H), 6.60 (s, 8H), 6.55 (s, 8H), 4.15–4.08 (m, 24H), 4.05 (t, *J* = 5.7 Hz, 8H), 4.01–3.99 (m, 8H), 3.84–3.80 (m, 16H), 3.60–3.57 (m, 8H), 3.37 (t, *J* = 6.1 Hz, 8H), 3.25 (s, 4H), 2.15 (m, 8H, overlap with HDO), 2.11 (s, 24H), 2.04 (s, 24H), 1.54 (s, 24H), 1.48–1.41 (m, 8H), 1.46 (s, 24H), 1.30–1.27 (m, 8H).

^{13}C NMR (150 MHz, CD_3CN, δ): 163.5, 163.3, 161.3, 161.1, 160.3, 159.9, 159.8, 157.7, 157.6, 156.8, 156.8, 156.5, 156.3, 153.4, 153.4, 153.0, 152.8, 152.1 (2 overlapping signals), 141.3, 141.2, 141.2, 141.1, 140.5, 140.3, 138.4, 138.3, 137.7 (2 overlapping signals), 137.6, 137.5, 137.0, 136.8, 136.7, 136.7, 134.5, 128.6, 128.5, 125.1, 125.0, 124.6, 124.5, 123.0, 122.8, 121.6, 121.5, 117.9, 117.8, 115.7, 115.1, 115.0, 114.8, 114.8, 114.5, 108.0, 107.8, 84.2, 77.5, 71.4, 70.3, 70.3, 69.8, 68.6, 68.6, 68.4, 65.2, 64.9, 30.3, 29.8, 26.5, 20.8, 20.7, 20.6, 20.5.

IR (film on NaCl, cm^{-1}): 3315*w*, 3281*w*, 2920*m*, 2853*w*, 2103*w*, 1604*s*, 1506*w*, 1455*s*, 1313*m*, 1278*w*, 1252*w*, 1161*w*, 1127*w*, 1072*w*, 1029*w*, 840*vs*, 809*m*, 734*w*, 557*m*.

HRMS (ESI) *m/z*: $[M\text{-}8PF_6]^{8+}$ calcd for $C_{344}H_{316}N_{24}O_{36}Ru_4$: 720.74705; found: 720.74979. $[M\text{-}7PF_6]^{7+}$ calcd for $C_{344}H_{316}F_6N_{24}O_{36}PRu_4$: 844.42016; found: 844.42169. $[M\text{-}6PF_6]^{6+}$ calcd for $C_{344}H_{316}F_{12}N_{24}O_{36}P_2Ru_4$: 1009.31765; found: 1009.31875.

Synthesis of the Threaded Ring-in-Ring Complex 1b



The exo/endo geometry of the orthogonal blue ligands undefined

A mixture of threaded macrocycle **13** (17.8 mg, 1.0 eq, 0.00560 mmol), mesylate Ru(II) cap **8c** (27.7 mg, 2.2 eq, 0.0125 mmol), anhydrous K_2CO_3 (20.1 mg, 26 eq, 0.146 mmol) and activated 4 Å molecular sieve powder (~30 mg) in anhydrous DMF (11 mL) under Ar atmosphere was heated to 70 °C for 34 h. Then the reaction temperature was increased to 78 °C, and the heating was continued for another 24 h. To the mixture additional mesylate Ru(II) cap **8c** (6.2 mg, 0.5 eq, 0.0028 mmol) in anhydrous DMF (1 mL) was added and the mixture was heated to 80 °C for 32 h. The reaction mixture was allowed to cool to room temperature, and sat. aq. KPF_6 was added. The resulting precipitate was collected by filtration over Celite, washed on the filter with excess water, Et_2O, hexane:EtOAc 3:1 and re-dissolved with acetonitrile into a clean flask. After evaporation of solvent the red residue was purified by silica gel column chromatography – first, a band containing a mixture of unreacted **8c** and hydrolysis product **8b** was moved by using 1st eluent (MeCN:CH_2Cl_2:H_2O:sat.KPF_6 139:11:5:1), then a band which contained the desired product **1b** (fractions controlled by on-flow ESI-MS) was moved by the 2nd eluent (MeCN:CH_2Cl_2:H_2O:sat.KPF_6 139:36:7:2). The fractions containing **1b** were evaporated and the residue was subjected to a 2nd column chromatography (eluent MeCN:CH_2Cl_2:H_2O:sat.KPF_6 139:47:4:0.4). The desired product moved as the first band. After evaporation of product fractions, the residue was dissolved in CH_2Cl_2, filtered and evaporated under reduced pressure to give the desired product **1b** (8.2 mg, 20%) as a red solid.

Mp: >250 °C dec.

^{1}H NMR (600 MHz, Acetone-d_6): 9.19-9.10 (m, 16H), 9.09-9.02 (m, 8H), 8.91-8.85 (m, 8H), 8.64-8.56 (m, 6H), 8.41-8.34 (m, 2H), 8.10 (s, 12H), 7.92 (dd, J = 8.2, 1.8 Hz, 4H), 7.55 (m, 4H), 7.39-7.36 (m, 8H), 7.20-7.12 (m, 12H), 6.91-6.90 (m, 8H), 6.73 (s, 8H), 6.72 (s, 8H), 6.70 (s, 8H), 6.57 (s, 8H), 4.18-4.14 (m, 32H), 4.06-4.05 (m,

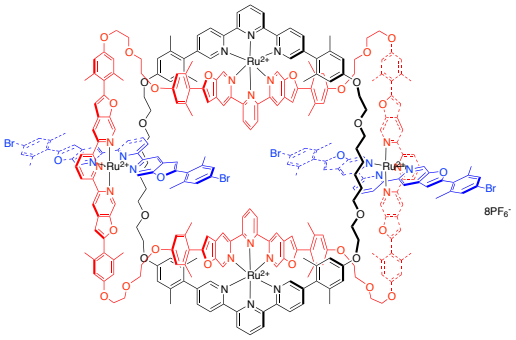
8H), 3.89-3.83 (m, 32H), 3.73-3.67 (m, 8H), 3.50-3.47 (m, 8H), 3.47 (s, 4H), 2.03 (s, 24H), 2.02 (s, 24H), 2.01 (s, 24H), 1.62-1.52 (m, 8H), 1.50 (s, 24H), 1.40-1.36 (m, 8H).

^{13}C NMR (150 MHz, Acetone-d_6): 163.1, 163.1, 161.6, 161.5, 161.2, 160.3, 159.8, 157.9, 157.3, 157.1, 157.0, 153.6, 152.9, 152.8, 152.8, 152.6, 141.2, 140.9, 140.9, 140.8, 140.3, 137.9, 137.9, 137.7, 137.6, 137.3, 137.2, 137.2, 137.0, 134.2, 128.4, 125.2, 124.7, 123.3, 123.2, 123.0, 121.3, 118.0, 115.6, 115.3, 115.1, 115.0, 114.8, 114.7, 107.9, 84.2, 77.7, 71.9, 71.7, 71.0, 71.0, 70.5, 70.4, 69.9, 68.6, 68.4, 30.3, 26.8, 20.8, 20.7, 20.7, 20.5.

IR (film on NaCl, cm^{-1}): 3315w, 3280w, 3122w, 3073w, 2924m, 2867w, 2103w, 1604s, 1505w, 1454s, 1383w, 1313m, 1291m, 1279m, 1252m, 1162m, 1128w, 1072w, 1005w, 841vs, 735w, 558m.

HRMS (ESI) *m/z*: $[M\text{-}8PF_6]^{8+}$ calcd for $C_{356}H_{324}N_{24}O_{44}Ru_4$: 755.75166; found: 755.75142; $[M\text{-}7PF_6]^{7+}$ calcd for $C_{356}H_{324}F_6N_{24}O_{44}PRu_4$: 884.42544; found: 884.42499; $[M\text{-}6PF_6]^{6+}$ calcd for $C_{356}H_{324}F_{12}N_{24}O_{44}P_2Ru_4$: 1055.99046; found: 1055.98883.

Synthesis of the Threaded Ring-in-Ring Complex 1c



The exo/endo geometry of the orthogonal blue ligands undefined

A mixture of threaded macrocycle **13** (5.48 mg, 1.0 eq, 0.001725 mmol), mesylate Ru(II) cap **9b** (3.38 mg, 1.0 eq, 0.001725 mmol) and anhydrous K_2CO_3 (5.96 mg, 25 eq, 0.0431 mmol) in anhydrous DMF (4.0 mL) under Ar atmosphere was heated to 75 °C for 18 h, and then an additional portion of mesylate **9b** (2.20 mg, 0.65 eq, 0.00112 mmol) in DMF (0.5 mL) was added. The heating of the mixture was continued for 8 h, after which the final portion of **9b** (2.20 mg, 0.65 eq, 0.00112 mmol) in DMF (0.5 mL) was added. The reaction mixture was heated for another 18 h, allowed to cool to room temperature and sat. aq. KPF_6 was added. The resulting red precipitate was

collected by filtration over Celite, washed on the filter with excess water, Et_2O, hexane:EtOAc 3:1 and re-dissolved with acetonitrile into a clean flask. After evaporation of solvent the red residue was purified by silica gel column chromatography (eluent MeCN:CH_2Cl_2:H_2O:aq.KPF_6 97:67:3:0.3). The combined product fractions were evaporated; the residue was treated with CH_2Cl_2 filtered and evaporated to give the product **1c** (4.7 mg, 41%) as a red solid.

Mp: >200 °C.

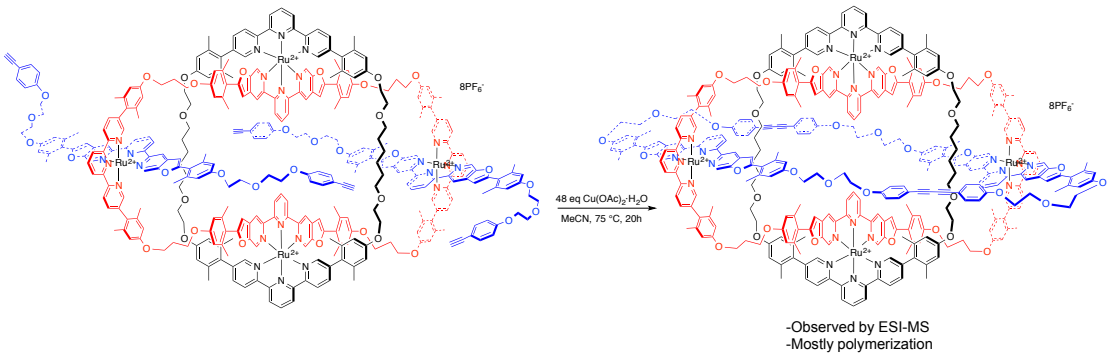
^{1}H NMR (600 MHz, Acetone-d_6): 9.10-9.05 (m, 16H), 8.99-8.93 (m, 8H), 8.79 (s, 4H), 8.78 (s, 4H), 8.54-8.46 (m, 6H), 8.28 (t, J = 8.1 Hz, 2H), 8.04 (s, 4H), 8.00 (s, 4H), 7.99 (s, 4H), 7.81 (dd, J = 8.3, 1.8 Hz, 4H), 7.45 (d, J = 1.5 Hz, 4H), 7.21 (s, 8H), 7.14 (s, 4H), 7.06 (s, 4H), 7.02 (s, 4H), 6.62 (s, 8H), 6.61 (s, 8H), 6.47 (s, 8H), 4.08-4.02 (m, 16H), 3.97-3.95 (m, 8H), 3.76-3.68 (m, 16H), 3.62-3.58 (m, 8H), 3.40-3.36 (m, 8H), 1.95 (overlap with signal of acetone-d_6, 48H), 1.91 (s, 24H), 1.50-1.42 (m, 8H), 1.40 (s, 24H), 1.29-1.26 (m, 8H).

^{13}C NMR (125 MHz, Acetone-d_6): 163.3, 163.2, 163.1, 163.1, 161.3, 159.8, 158.0, 157.1, 157.1, 157.0, 156.6, 153.6, 153.1, 153.0, 152.9, 152.8, 152.6, 141.6, 141.3, 140.9, 140.9, 140.8, 138.0, 137.9, 137.8, 137.6, 137.6, 137.4, 137.3, 137.3, 137.3, 137.1, 137.1, 131.5, 128.4, 128.3, 125.2, 125.0, 124.7, 123.3, 123.2, 123.2, 121.4, 121.3, 118.3, 118.1, 114.9, 114.7, 114.7, 108.6, 108.0, 107.8, 71.9, 70.5, 70.4, 69.9, 68.7, 68.5, 68.1, 29.2, 26.9, 20.8, 20.7, 20.5, 20.3.

IR (film on NaCl, cm^{-1}): 3091*w*, 2957*w*, 2919*w*, 2853*w*, 1603*m*, 1313*m*, 1280*m*, 1263*m*, 1163*m*, 1009*w*, 842*s*, 807*m,* 701*w*, 558*w*.

HRMS (ESI) *m/z*: $[M]^{8+}$ calcd for $C_{308}H_{272}Br_4N_{24}O_{32}Ru_4$: 692.66692; found: 692.66787; $[M+PF_6]^{7+}$ calcd for $C_{308}H_{272}Br_4F_6N_{24}O_{32}PRu_4$: 812.32858; found: 812.32970.

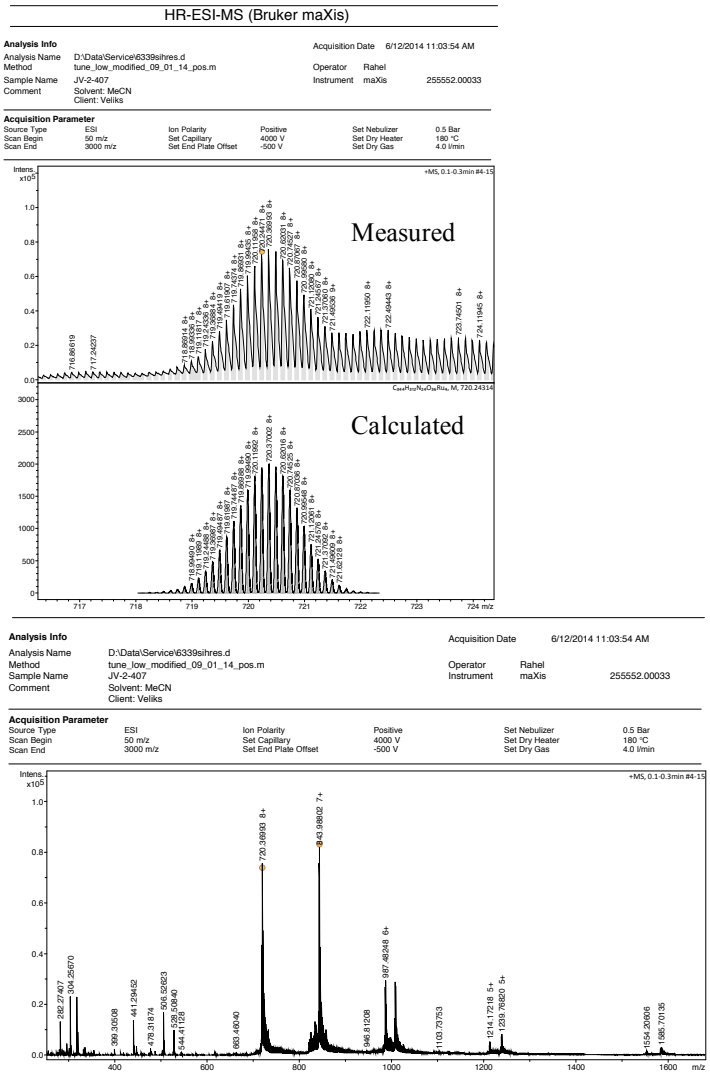
Macrocyclization attempts to form the Borromean link ruthenium(II) complex 14



A mixture of threaded ring-in-ring Ru(II) complex **1a** (0.73 mg, 1.0 eq, 0.000105 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1.01 mg, 48 eq, 0.00506 mmol) in acetonitrile (3.0 mL) was heated to reflux for 20 h. The reaction mixture was allowed to cool to room temperature, and the solvent was evaporated under reduced pressure. The resulting brown residue was re-dissolved in a minimum amount of acetonitrile and re-precipitated by carefully transferring it with a Pasteur pipette to the conc. aq. KPF_6, which was placed over the Celite fitted in a small frit filter. The resulting red precipitate was filtered over Celite, washed on the filter with excess water, and re-dissolved into a clean flask. After evaporation of solvent, a red solid was obtained (0.46 mg), which was subjected to silica gel column chromatography (in Pasteur pipette) (eluent MeCN:CH_2Cl_2:H_2O:aq.KPF_6 97:100:3:0.3). The fractions were analyzed by on-flow ESI-MS. The fractions containing the product **14** were evaporated to give less then 0.2 mg of red solid which was subjected to HR-ESI-MS.

HRMS (ESI) *m/z*: $[M\text{-}8PF_6]^{8+}$ calcd for $C_{344}H_{312}N_{24}O_{36}Ru_4$: 720.24314; found: 720.24471. $[M\text{-}7PF_6]^{7+}$ calcd for $C_{344}H_{312}F_6N_{24}O_{36}PRu_4$: 843.84426; found: 843.84523.

HR-ESI-MS (Bruker maXis)



Analysis Info
Analysis Name D:\Data\Service\6339sihres.d
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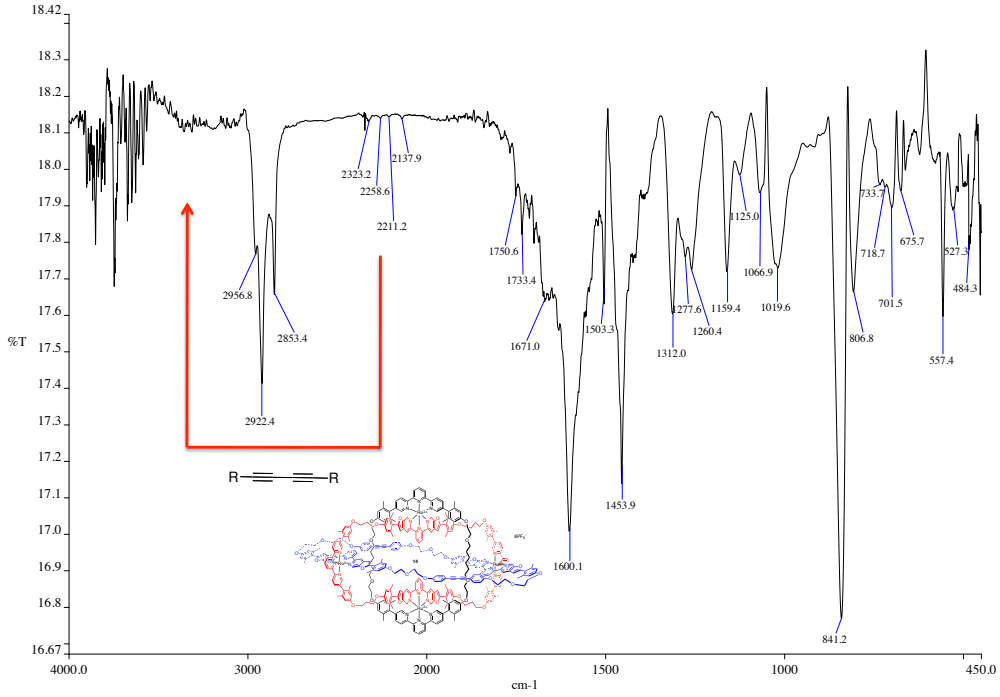
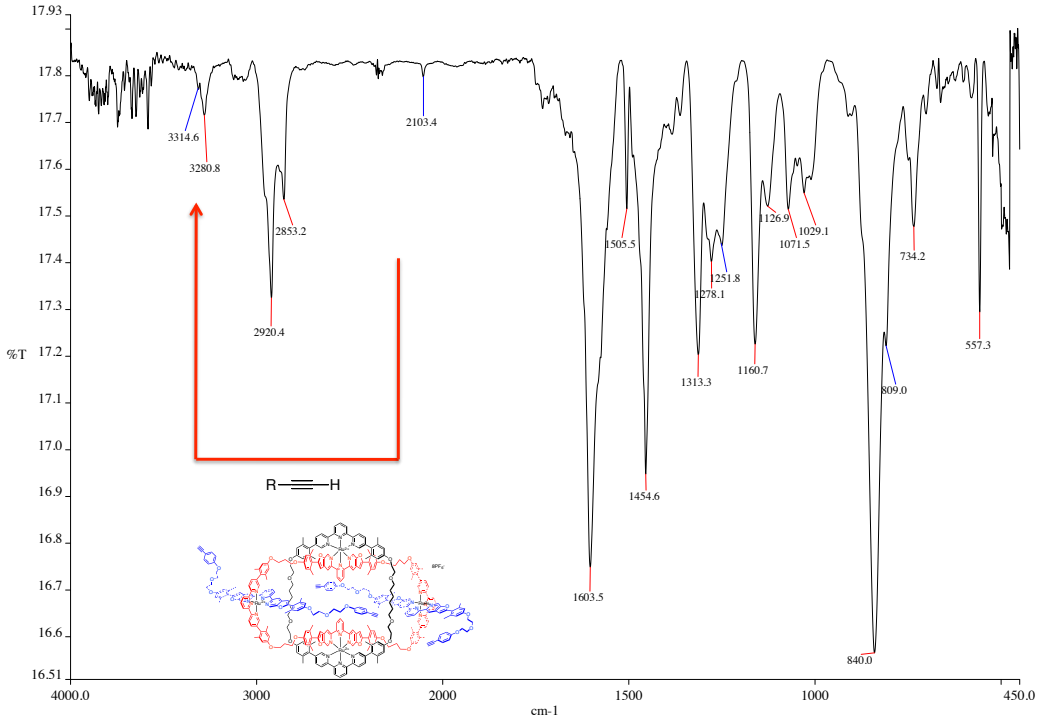
Sample Name JV-2-407
Comment Solvent: MeCN
Client: Veliks
Acquisition Date 6/12/2014 11:03:54 AM
Operator Rahel
Instrument maXis 255552.00033
Acquisition Parameter
Source Type ESI
Scan Begin 50 m/z
Scan End 3000 m/z
Ion Polarity Positive
Set Capillary 4000 V
Set End Plate Offset -500 V
Set Nebulizer 0.5 Bar
Set Dry Heater 180 °C
Set Dry Gas 4.0 l/min

HR-ESI-MS (Bruker maXis)

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
720.24471	1	C344H312N24O36Ru4	720.24314	0.36	132.4	1	100.00	203.0	even	ok
843.84523	1	C344H312F6N24O36PRu4	843.84426	1.34	126.1	1	100.00	200.5	even	ok





[1] J. Veliks, J.-C. Tseng, K. I. Arias, F. Weisshar, A. Linden, J. S. Siegel, *Chem. Sci.* **2014**, *5*, 4317-4327.

[2] D. L. Pearson, J. M. Tour, *J. Org. Chem.* **1997**, *62*, 1376-1387.

[3] J. Veliks, O. Blacque, J. S. Siegel, *Inorg. Chem.* **2014**, *53*, 12122-12126.

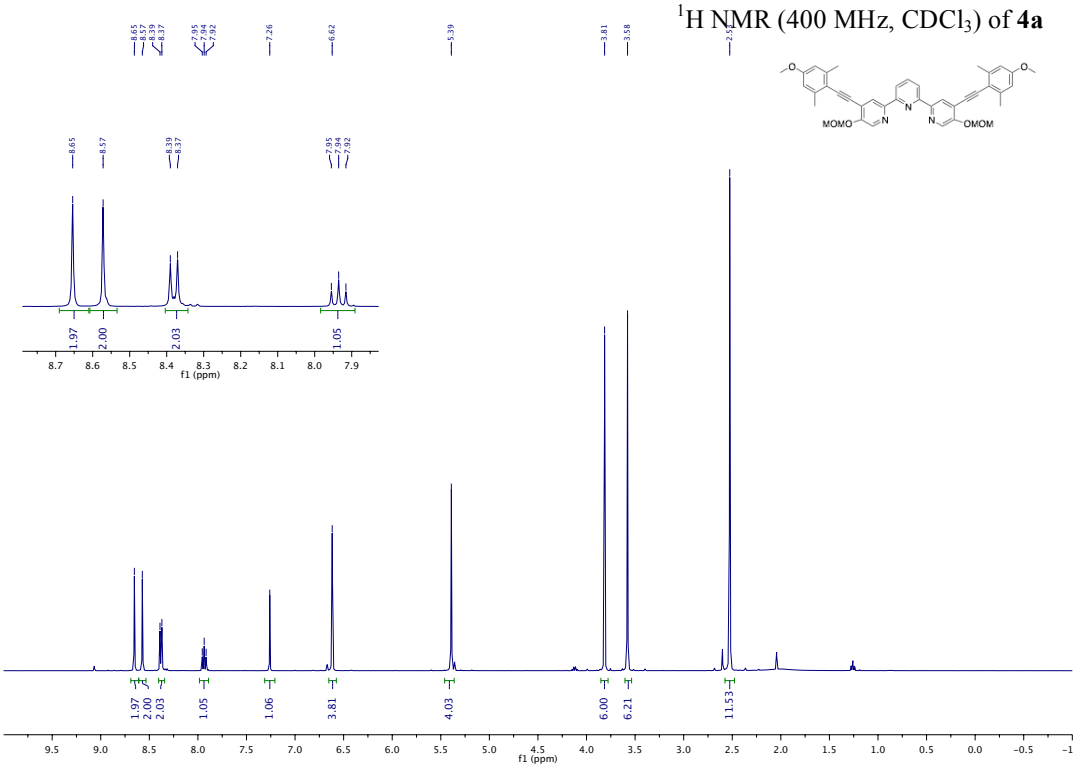
[4] J. C. Loren, J. S. Siegel, *Angew. Chem. Int. Ed.* **2001**, *40*, 754-757.

[5] aD. James, J.-M. Escudier, E. Amigues, J. Schulz, C. Vitry, T. Bordenave, M. Szlosek-Pinaud, E. Fouquet, *Tetrahedron Lett.* **2010**, *51*, 1230-1232; bR. Chandra, S. Oya, M. P. Kung, C. Hou, L. W. Jin, H. F. Kung, *J. Med. Chem.* **2007**, *50*, 2415-2423.

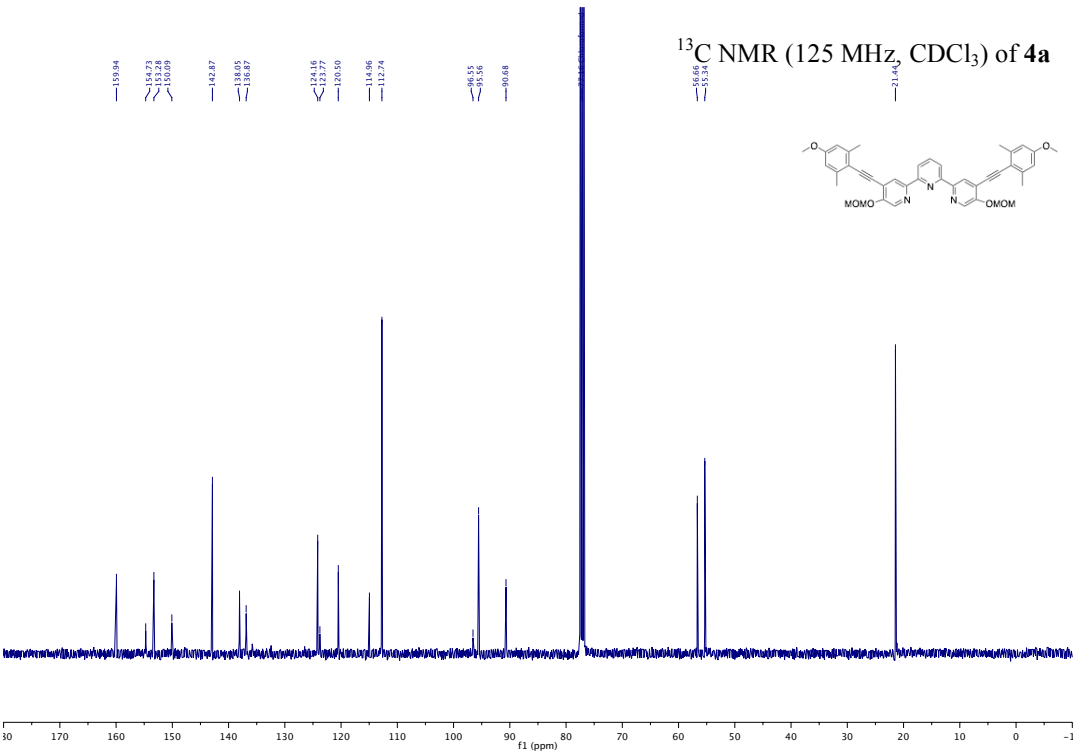
[6] J. C. Loren, M. Yoshizawa, R. F. Haldimann, A. Linden, J. S. Siegel, *Angew. Chem. Int. Ed.* **2003**, *42*, 5702-5705.

3. NMR spectra

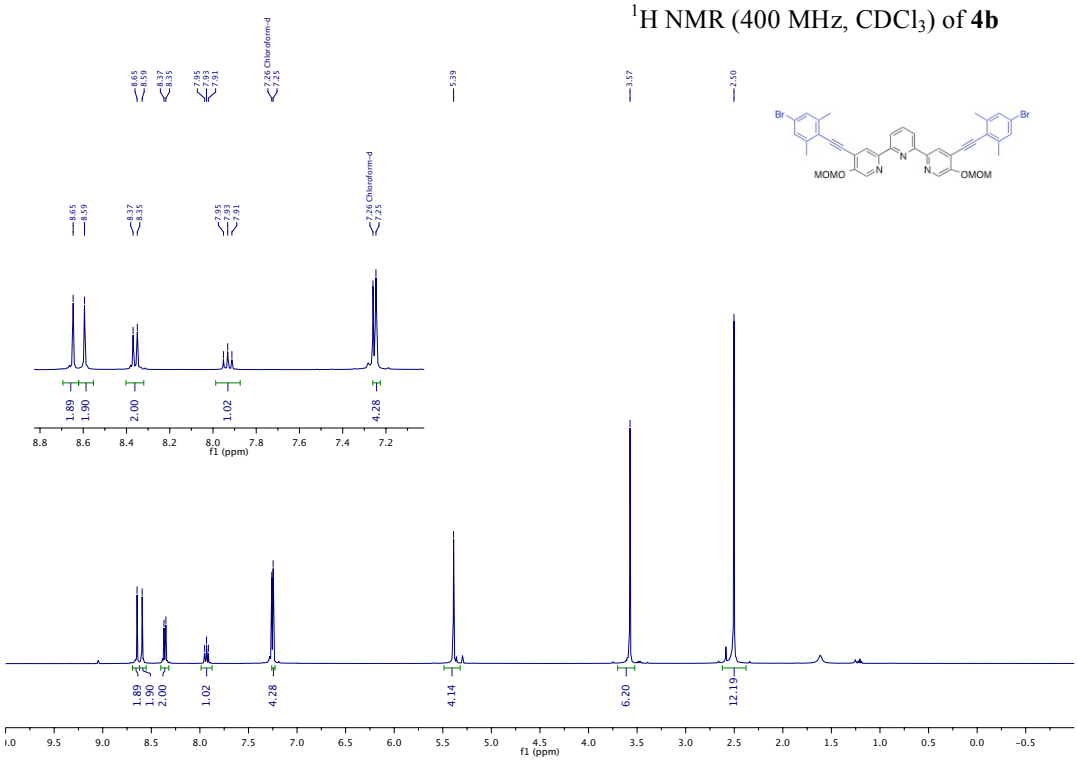
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



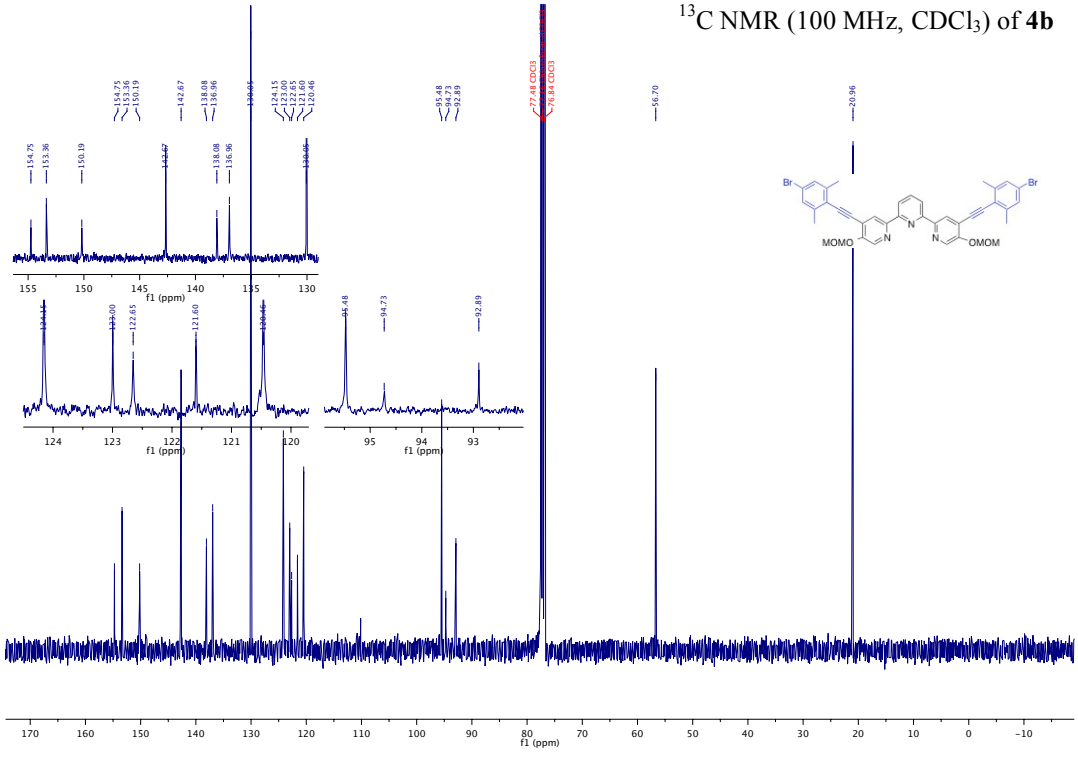
^{13}C NMR (125 MHz, $CDCl_3$) of **4a**



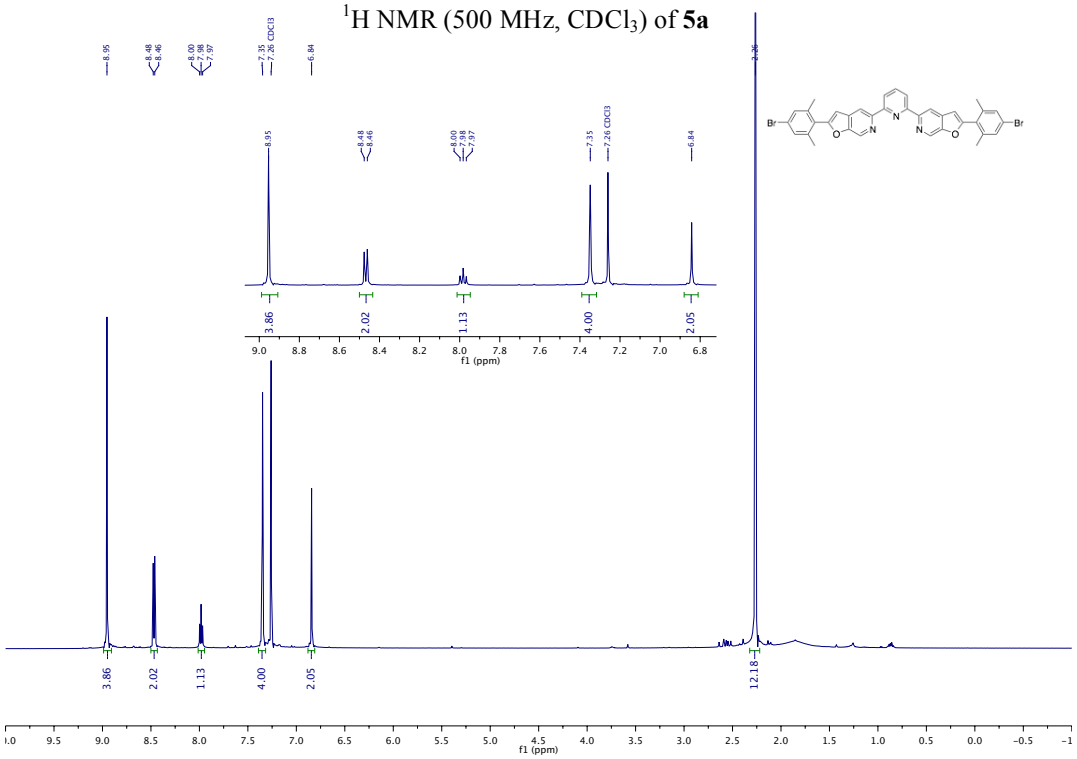
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



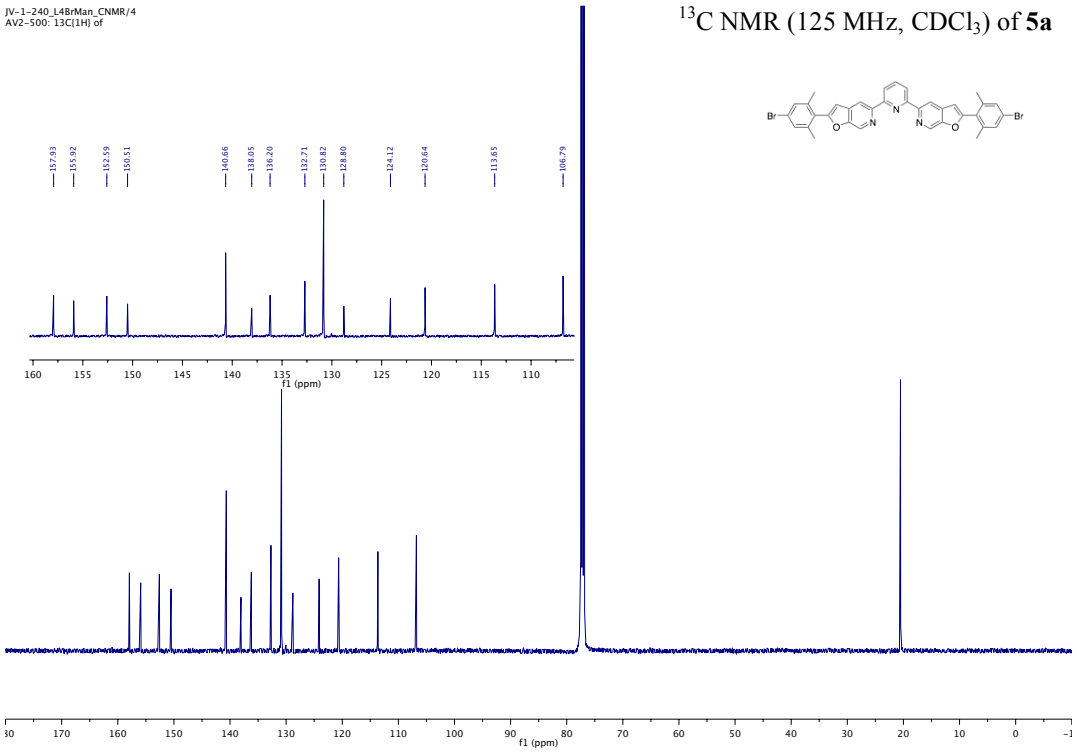
^{13}C NMR (100 MHz, $CDCl_3$) of **4b**



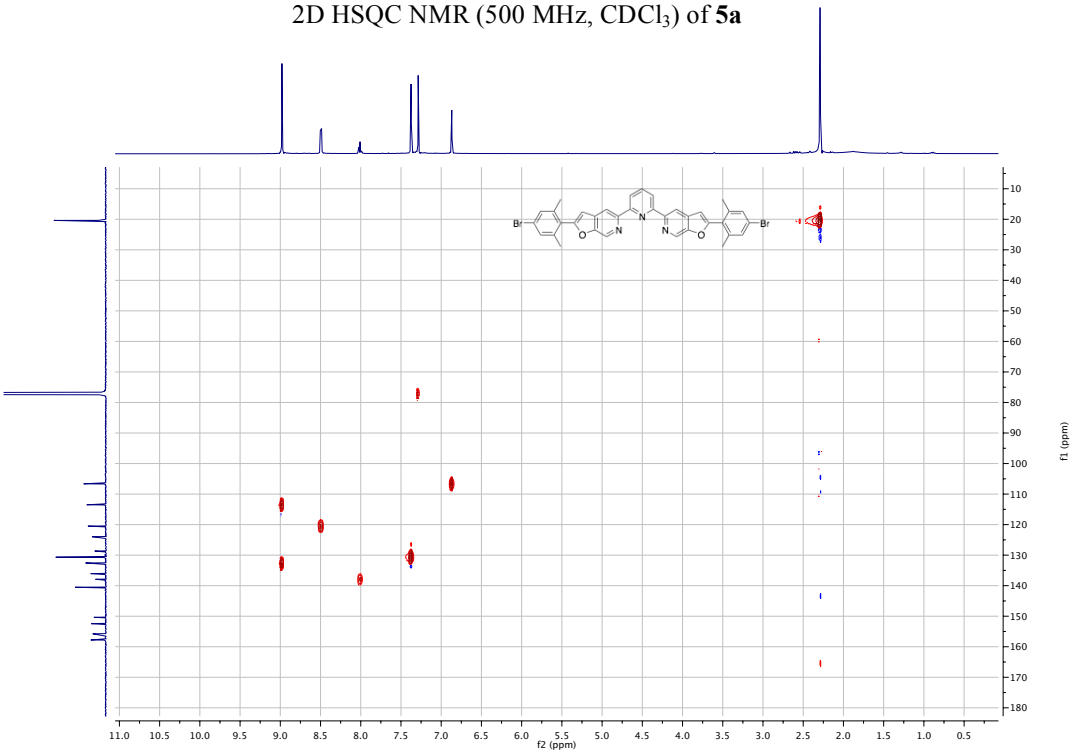
^{1}H NMR (500 MHz, $CDCl_3$) of **5a**



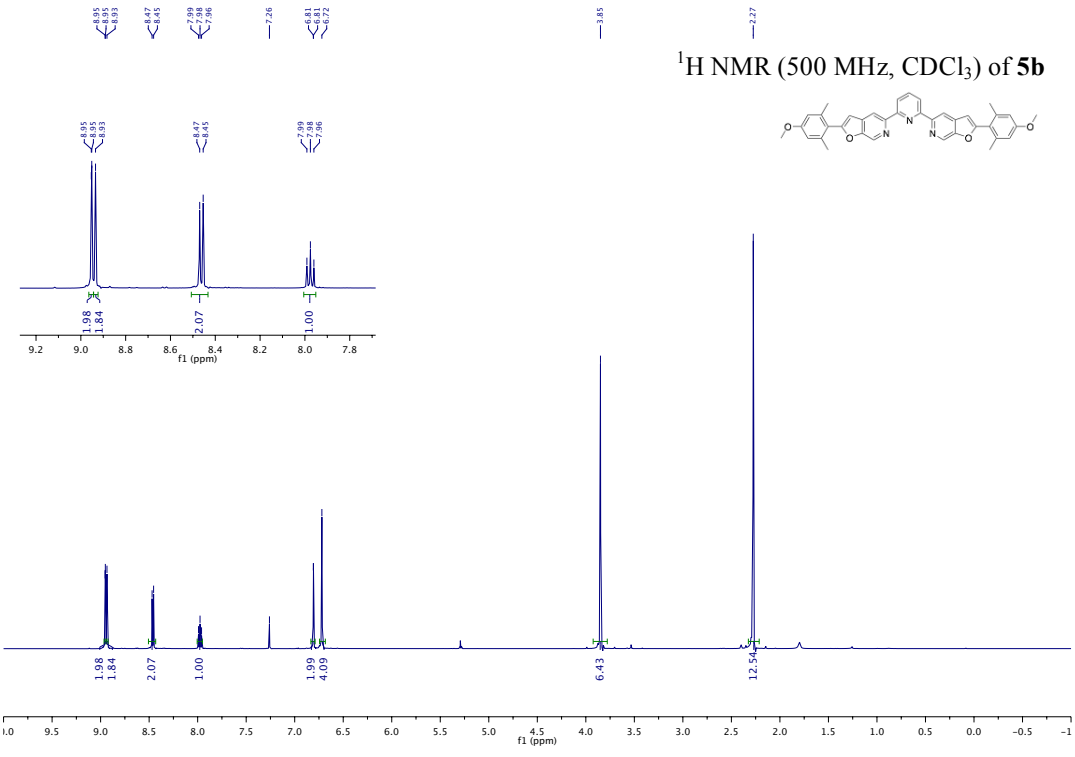
^{13}C NMR (125 MHz, $CDCl_3$) of **5a**



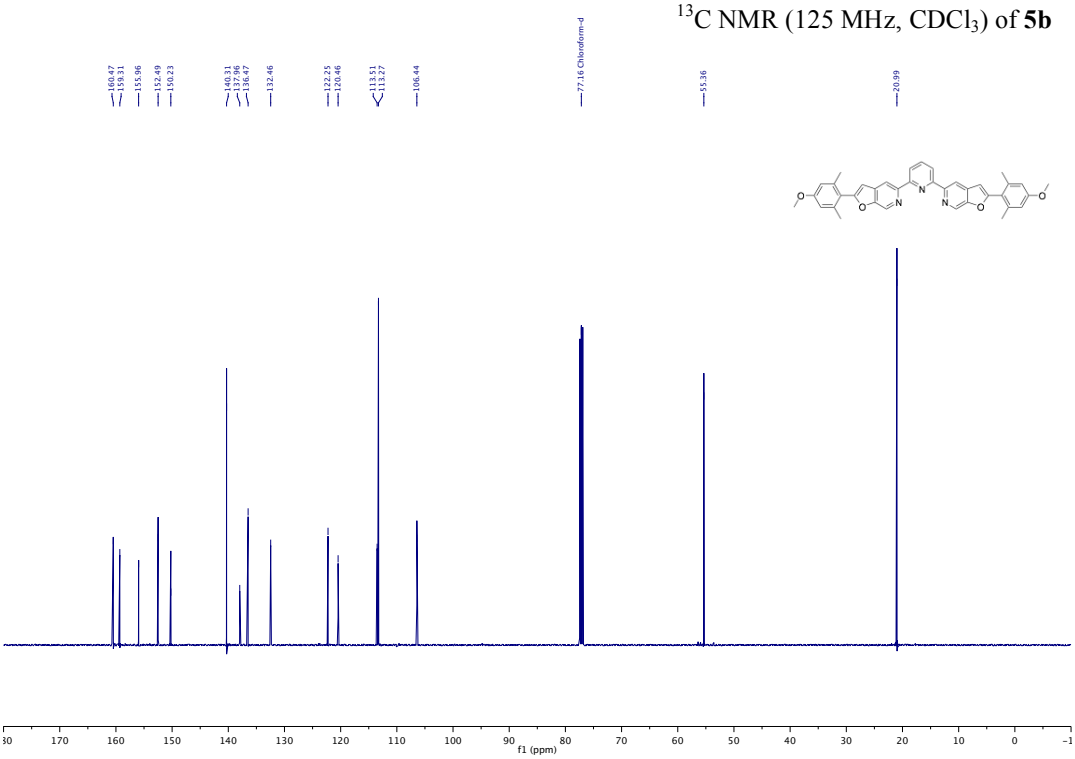
2D HSQC NMR (500 MHz, $CDCl_3$) of **5a**



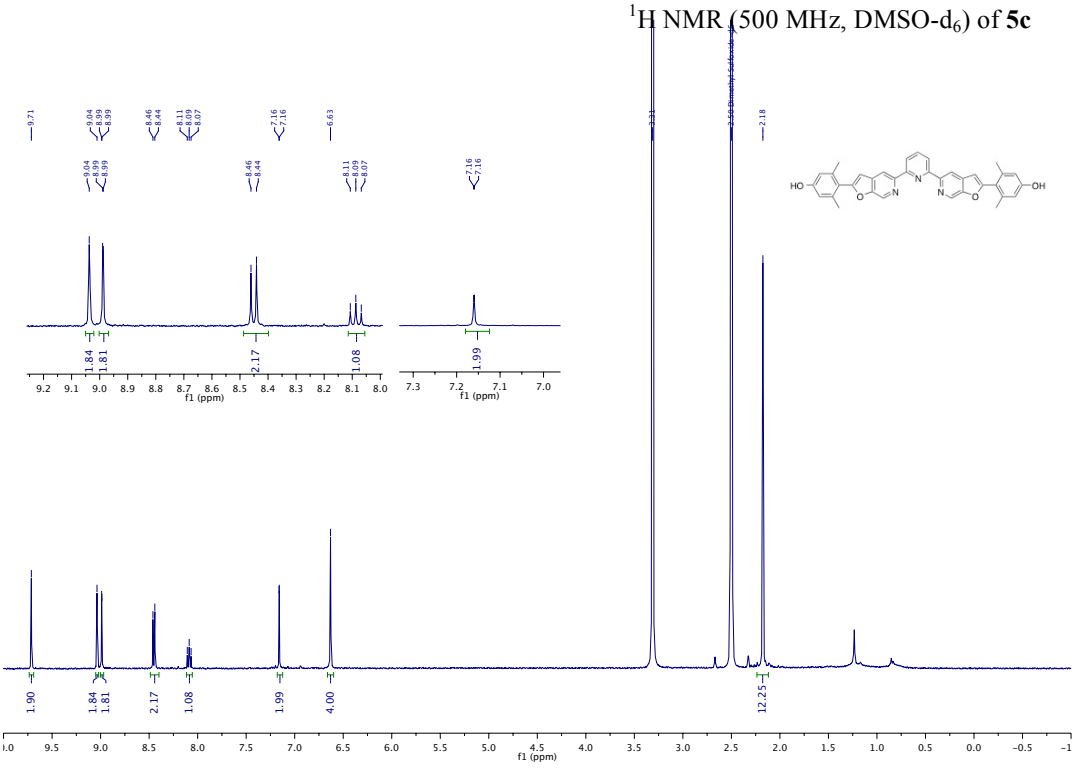
^{1}H NMR (500 MHz, $CDCl_3$) of **5b**



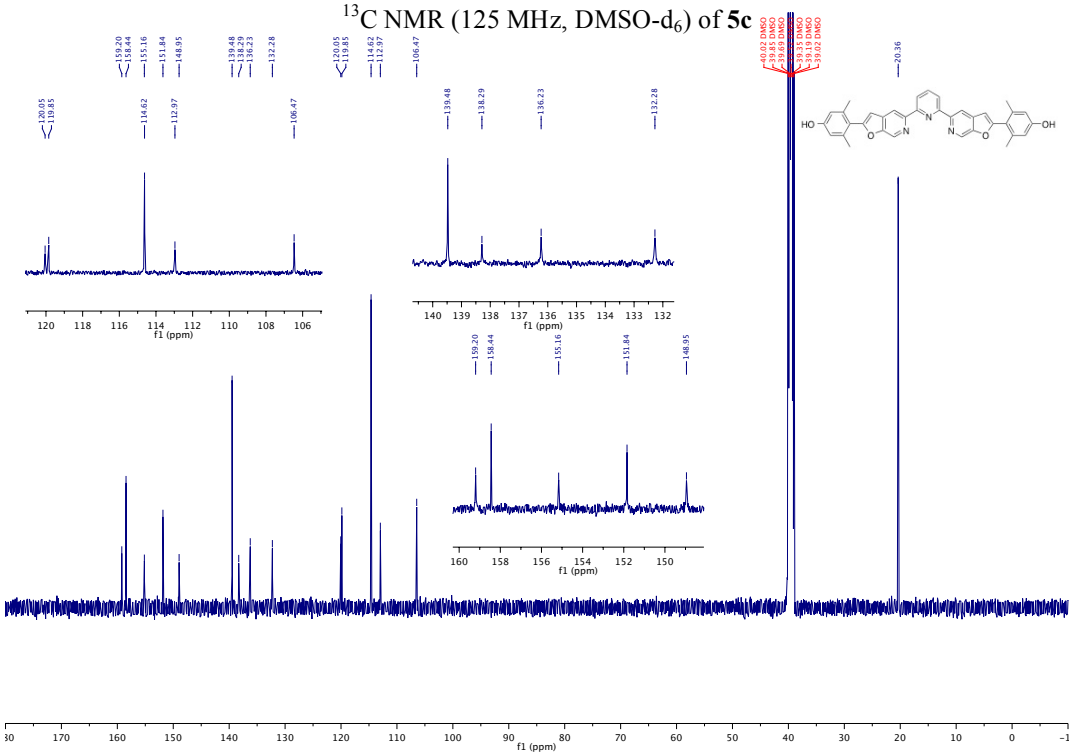
^{13}C NMR (125 MHz, $CDCl_3$) of **5b**



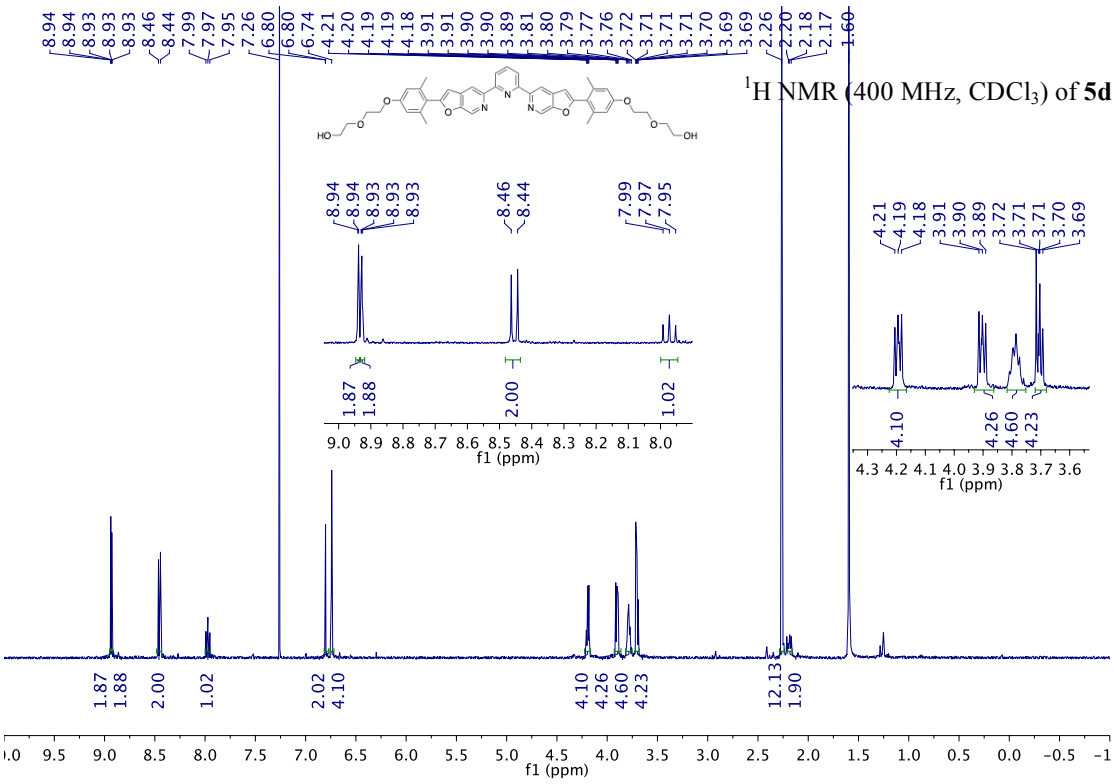
^{1}H NMR (500 MHz, DMSO-d_6) of **5c**



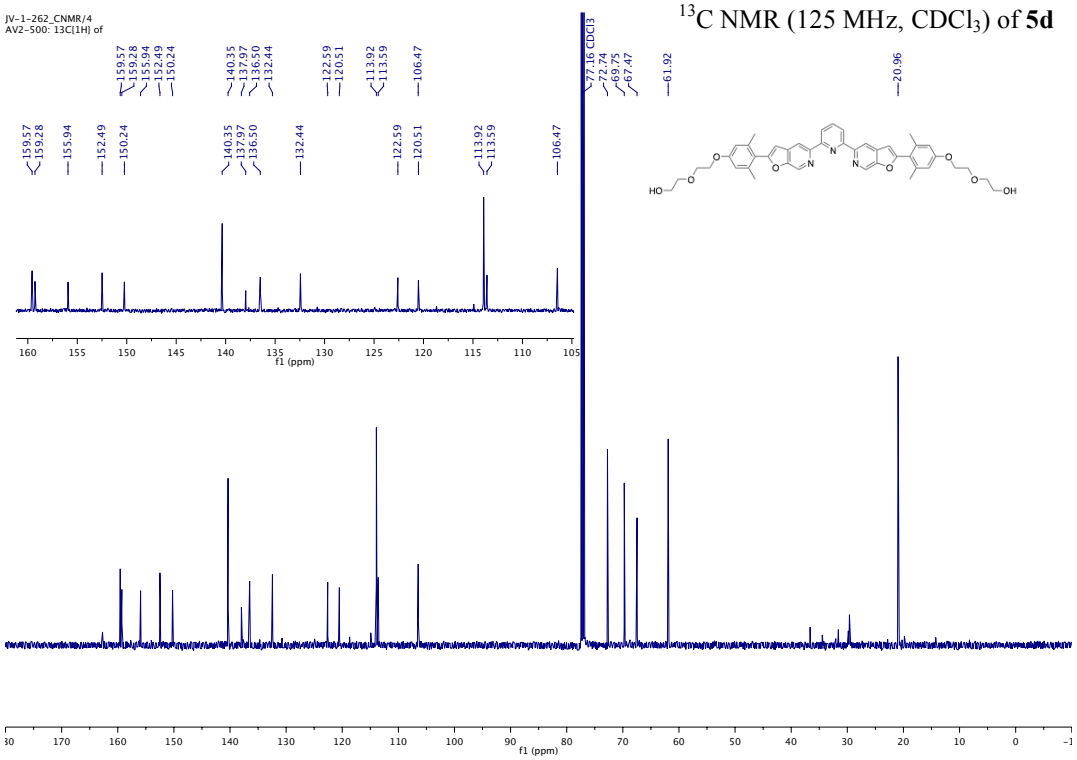
^{13}C NMR (125 MHz, DMSO-d$_6$) of **5c**



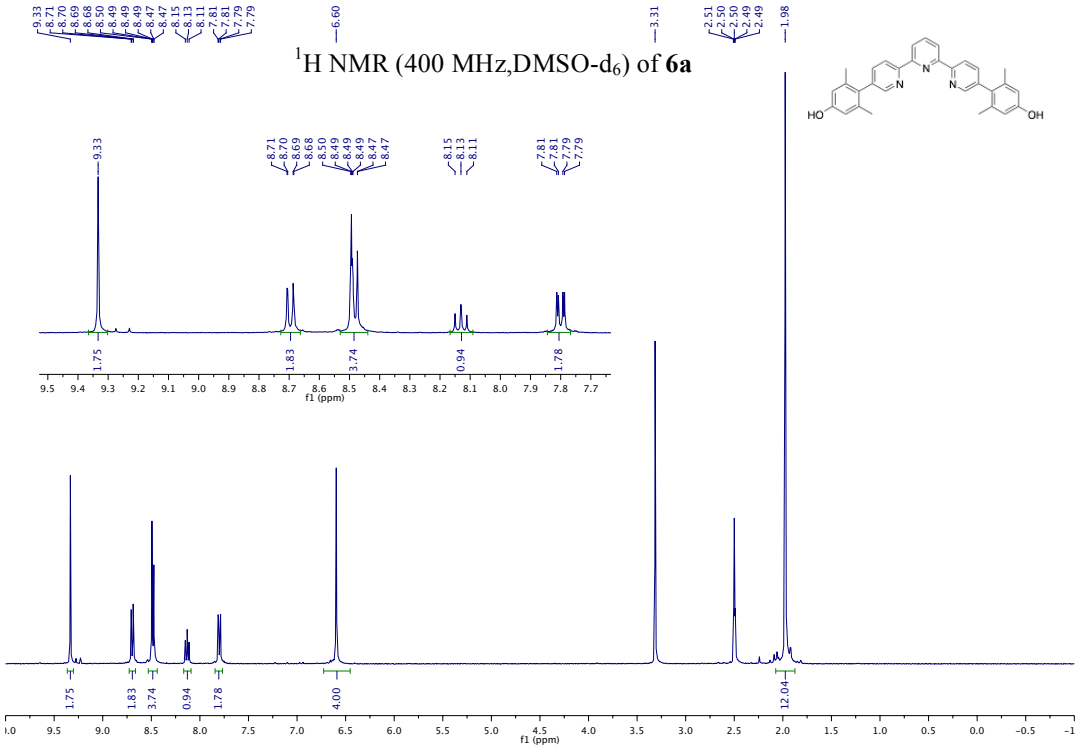
^{1}H NMR (400 MHz, CDCl$_3$) of **5d**



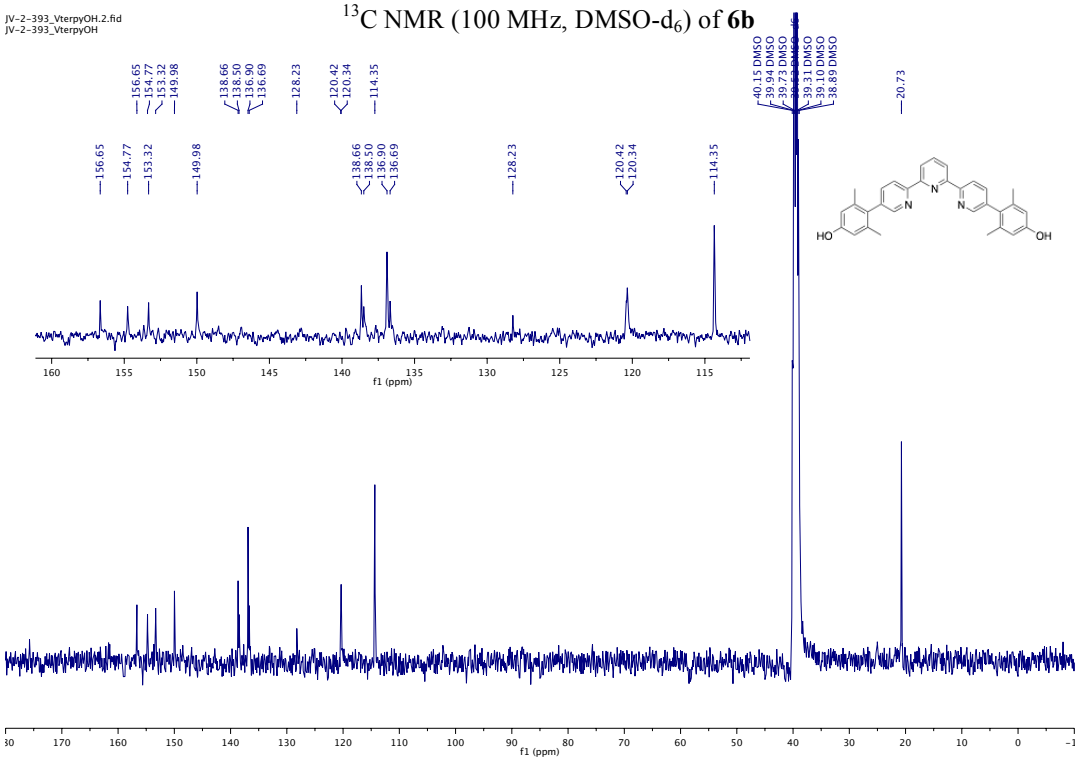
^{13}C NMR (125 MHz, $CDCl_3$) of **5d**



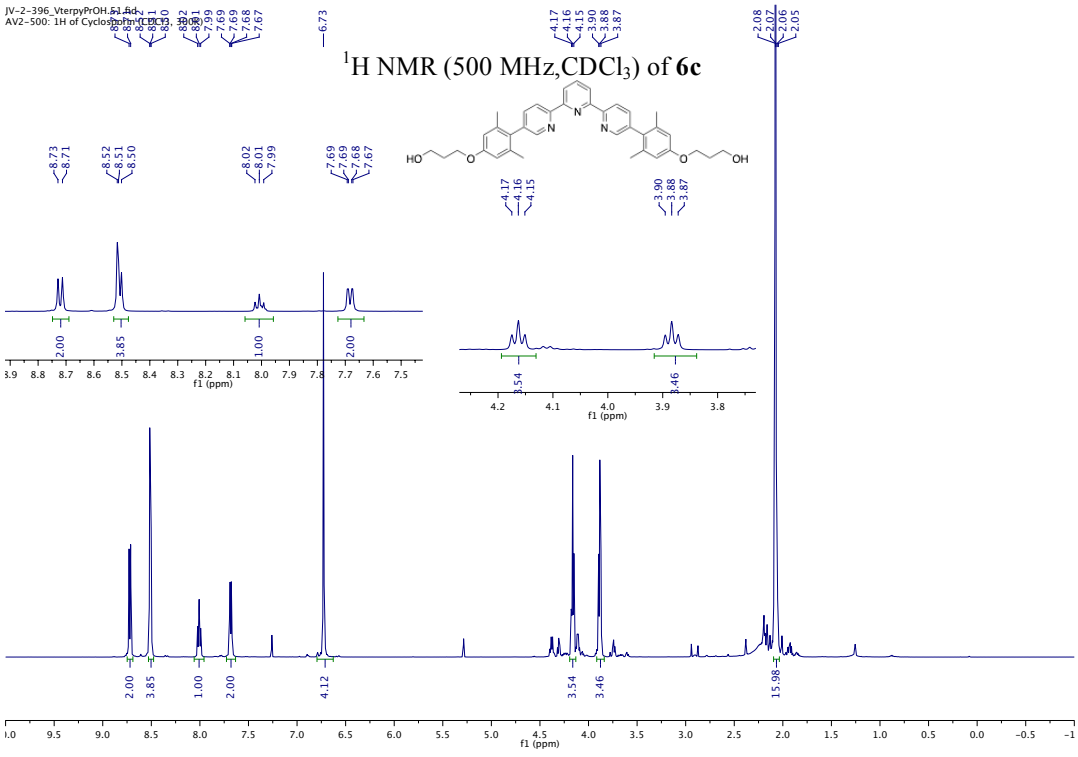
^{1}H NMR (400 MHz,DMSO-d_6) of **6a**



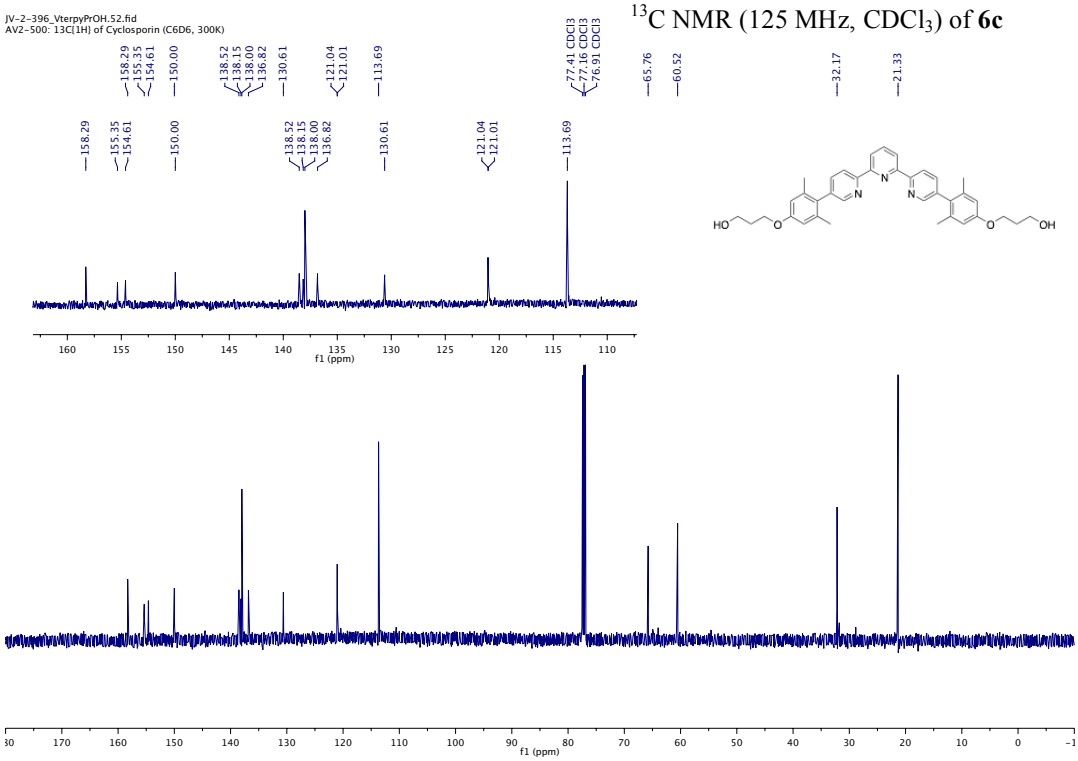
^{13}C NMR (100 MHz, DMSO-d$_6$) of **6b**



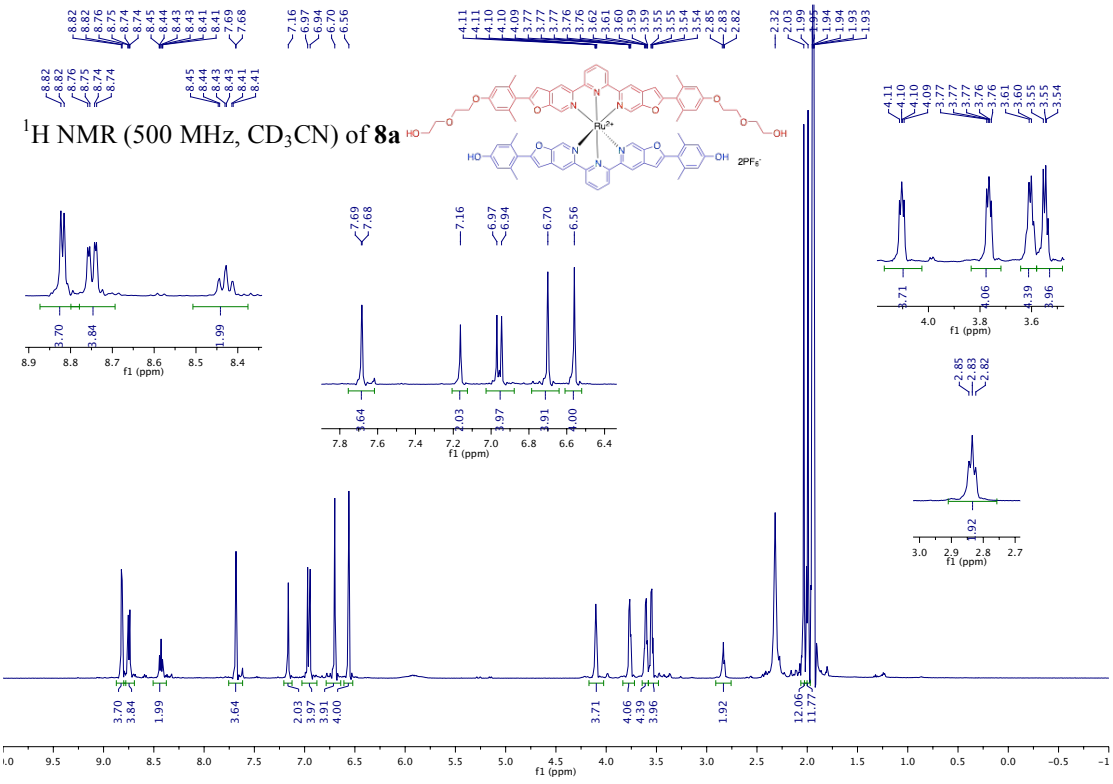
^{1}H NMR (500 MHz,CDCl$_3$) of **6c**



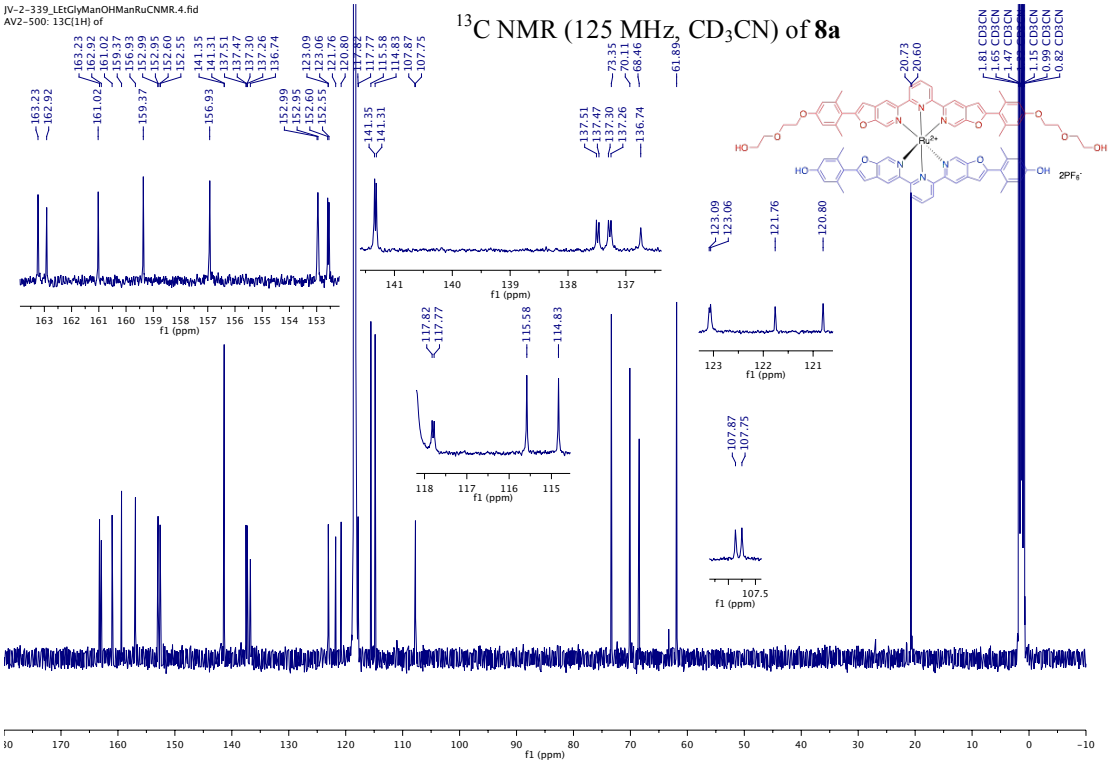
^{13}C NMR (125 MHz, $CDCl_3$) of **6c**



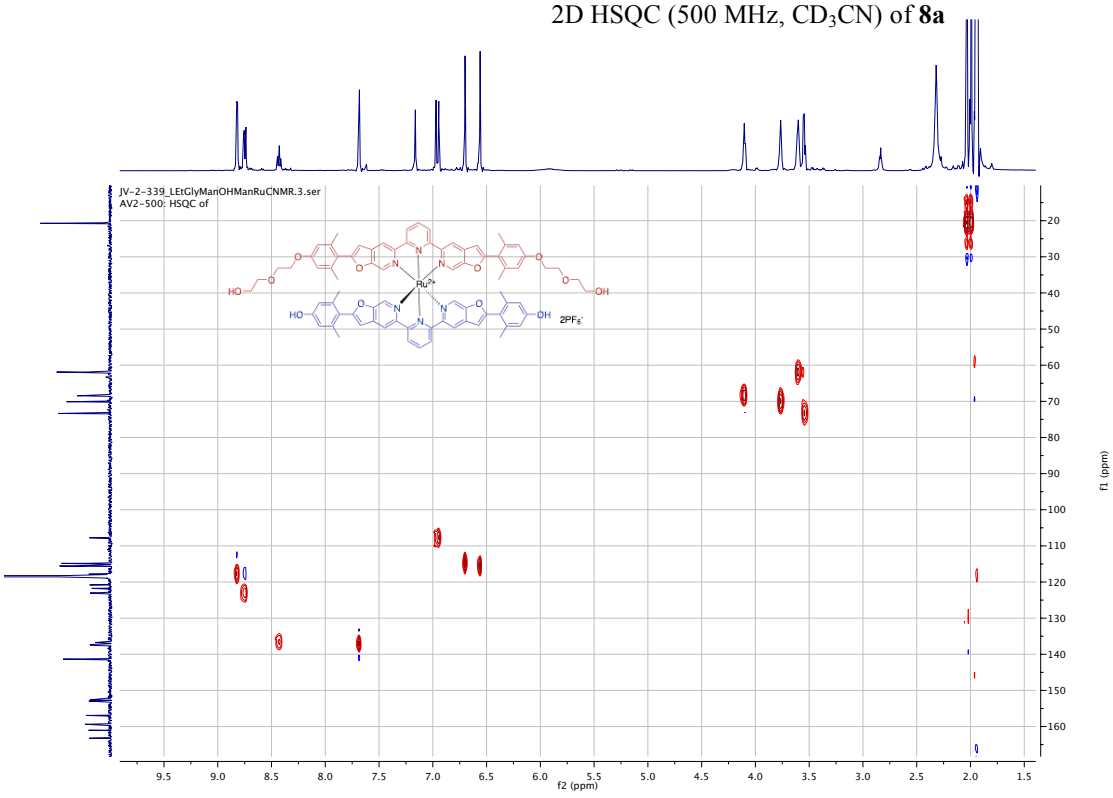
^{1}H NMR (500 MHz, CD_3CN) of **8a**

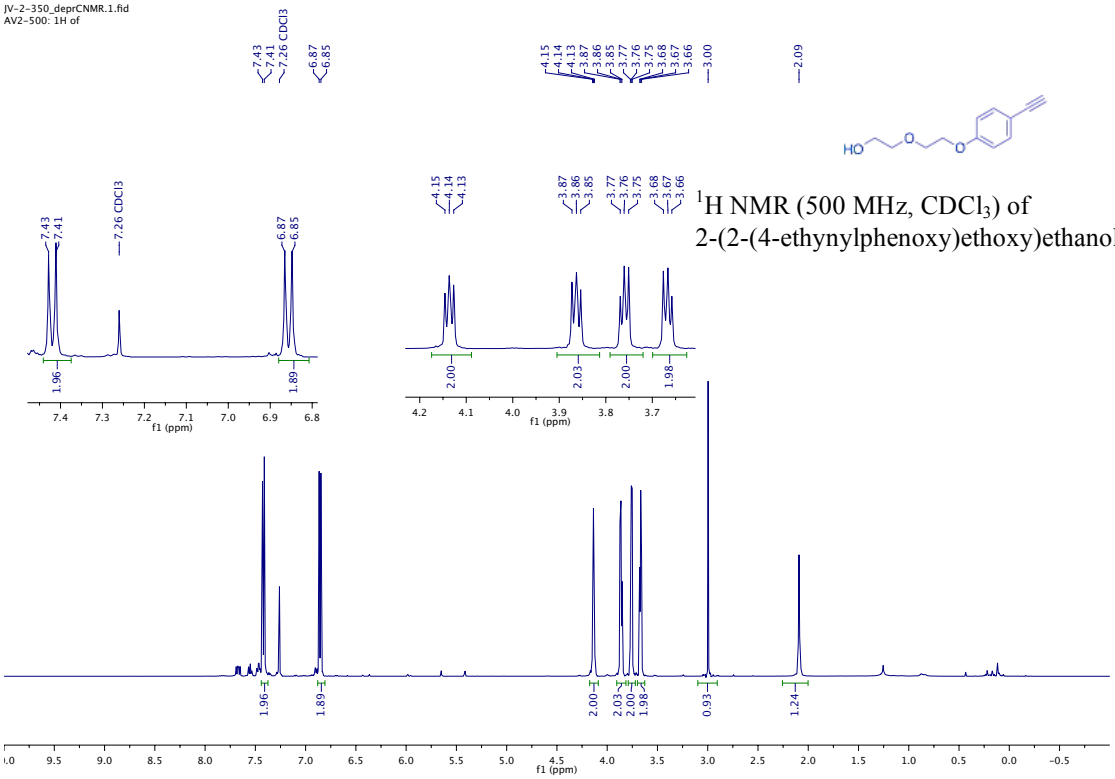


^{13}C NMR (125 MHz, CD_3CN) of **8a**

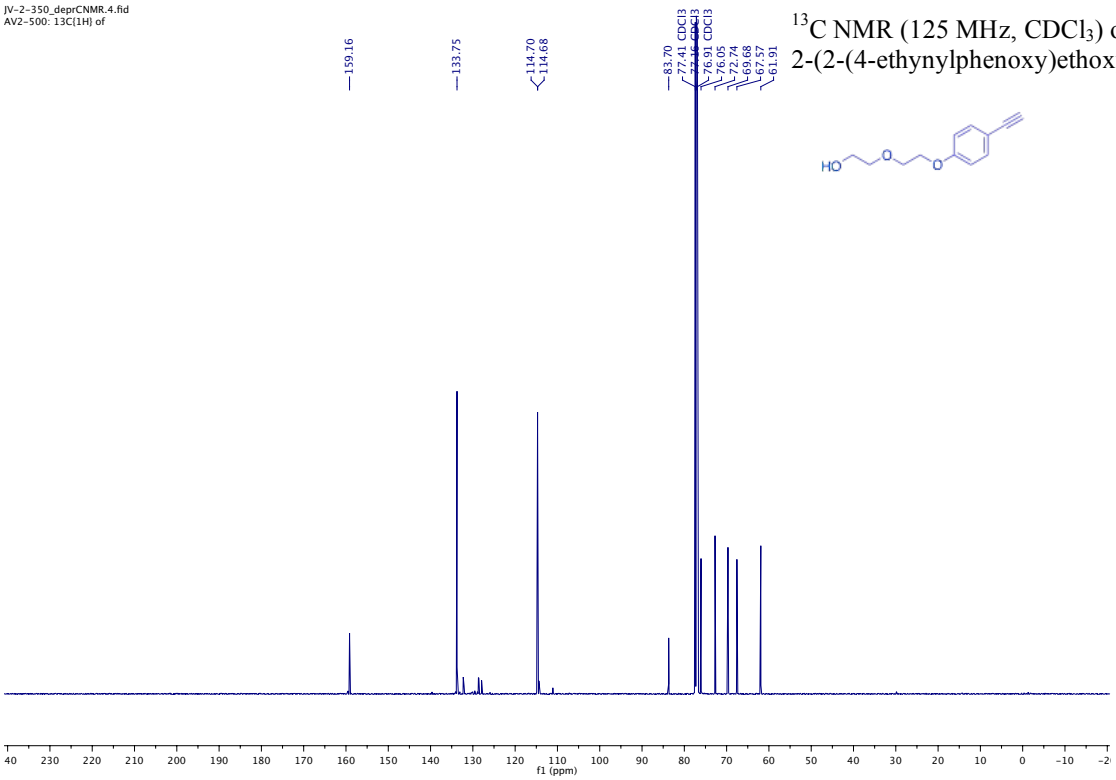


2D HSQC (500 MHz, CD_3CN) of **8a**

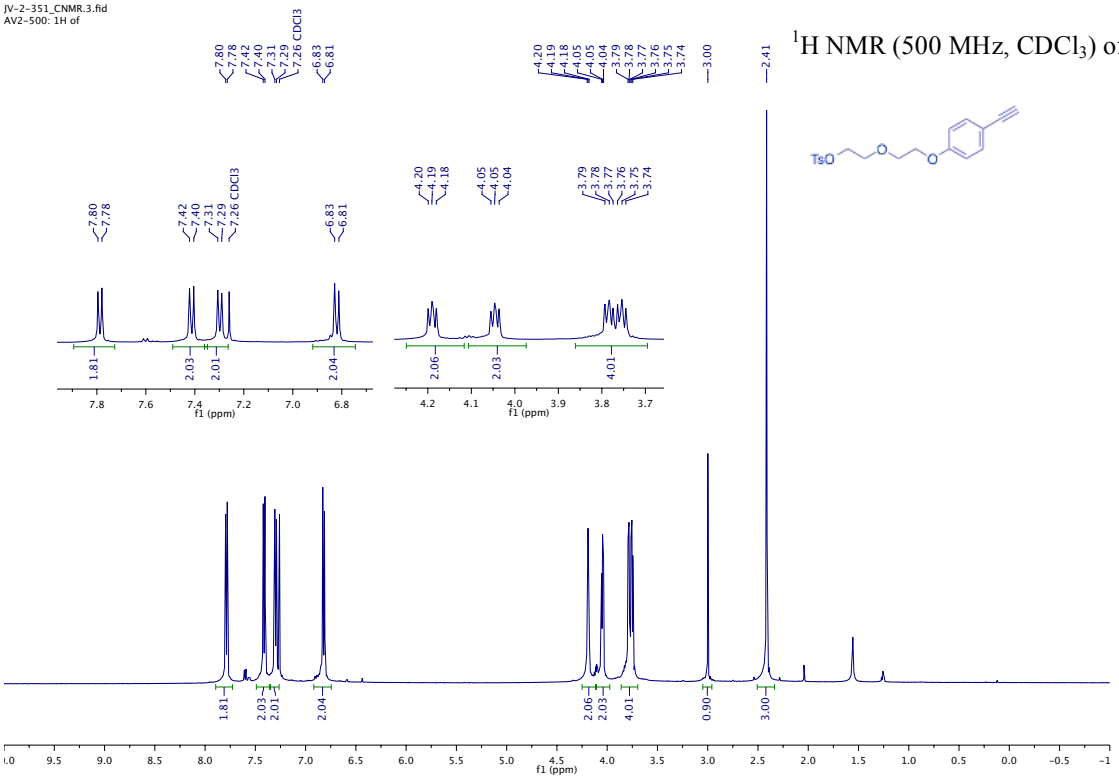




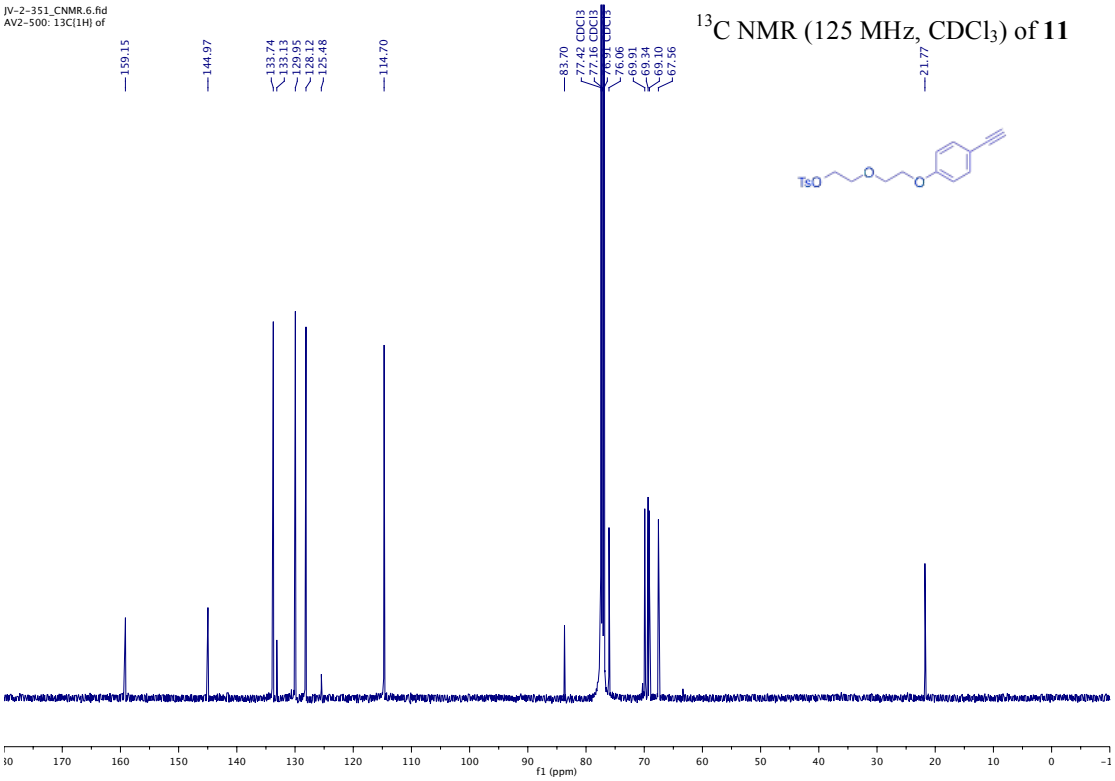
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(2-(4-ethynylphenoxy)ethoxy)ethanol



^{13}C NMR (125 MHz, $CDCl_3$) of 2-(2-(4-ethynylphenoxy)ethoxy)ethanol

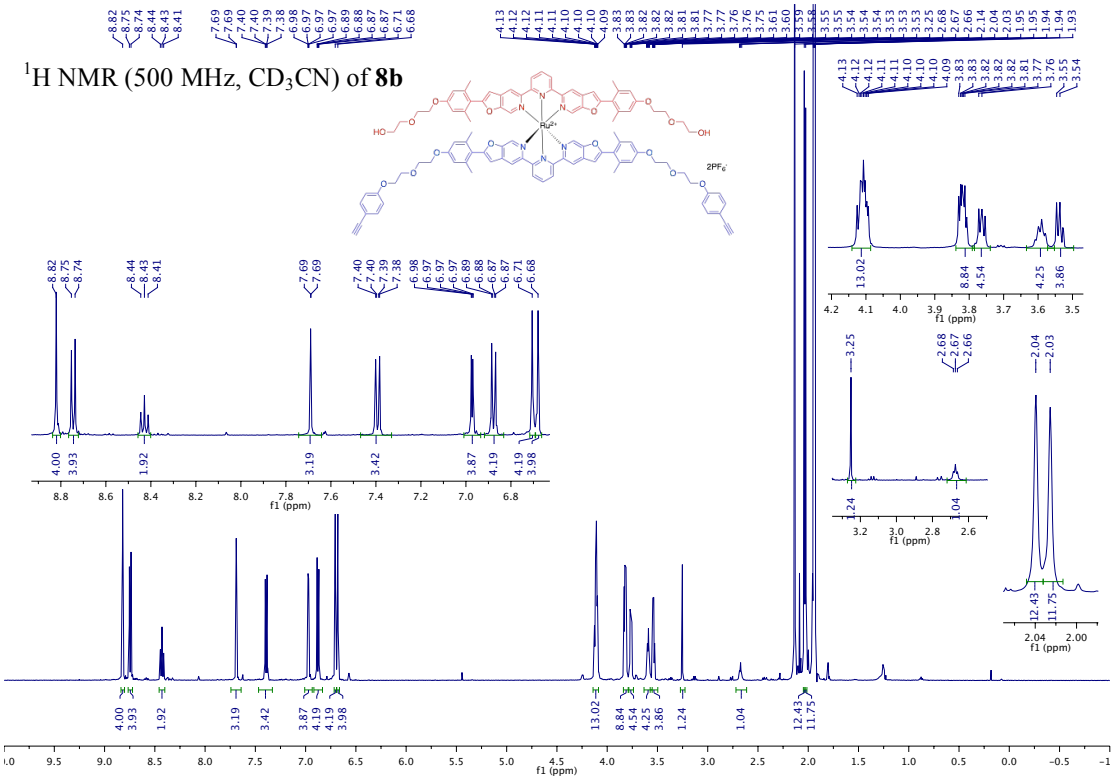


^{1}H NMR (500 MHz, $CDCl_3$) of **11**

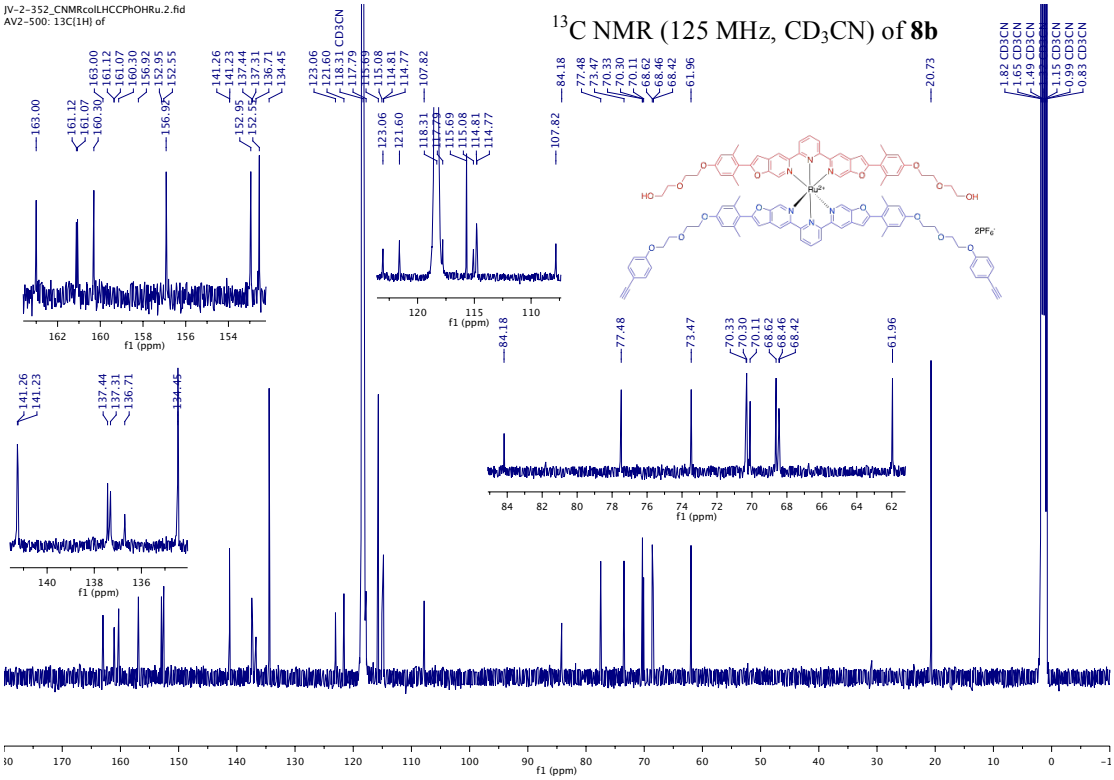


^{13}C NMR (125 MHz, $CDCl_3$) of **11**

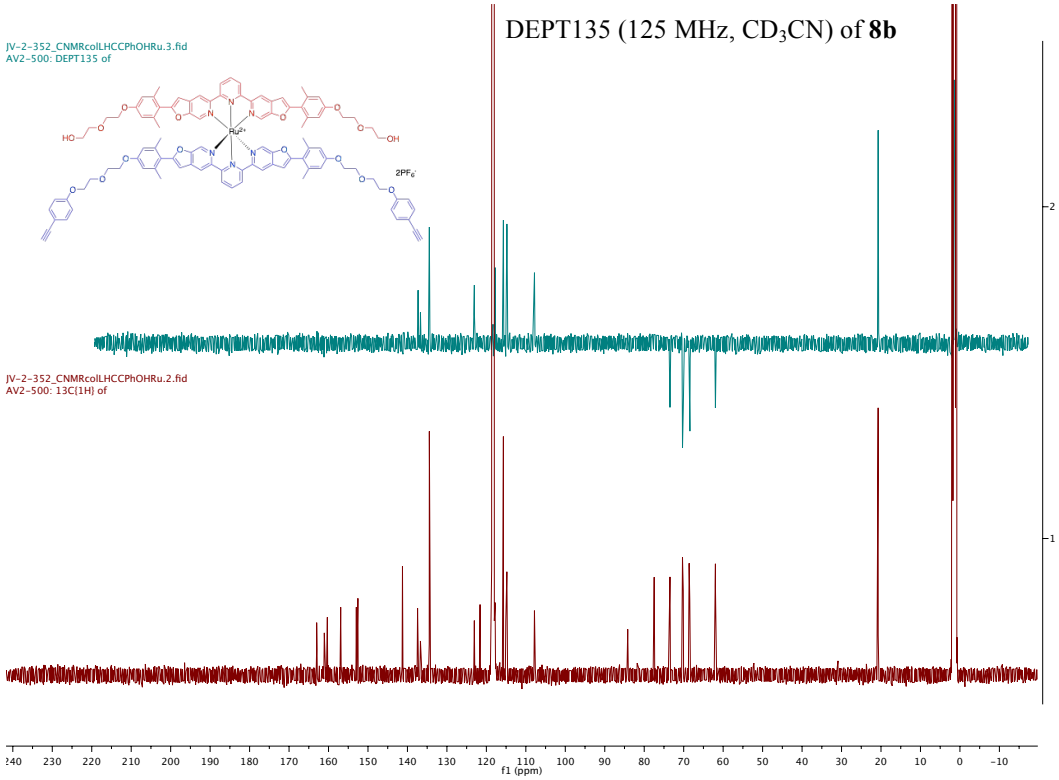
^{1}H NMR (500 MHz, CD_3CN) of **8b**

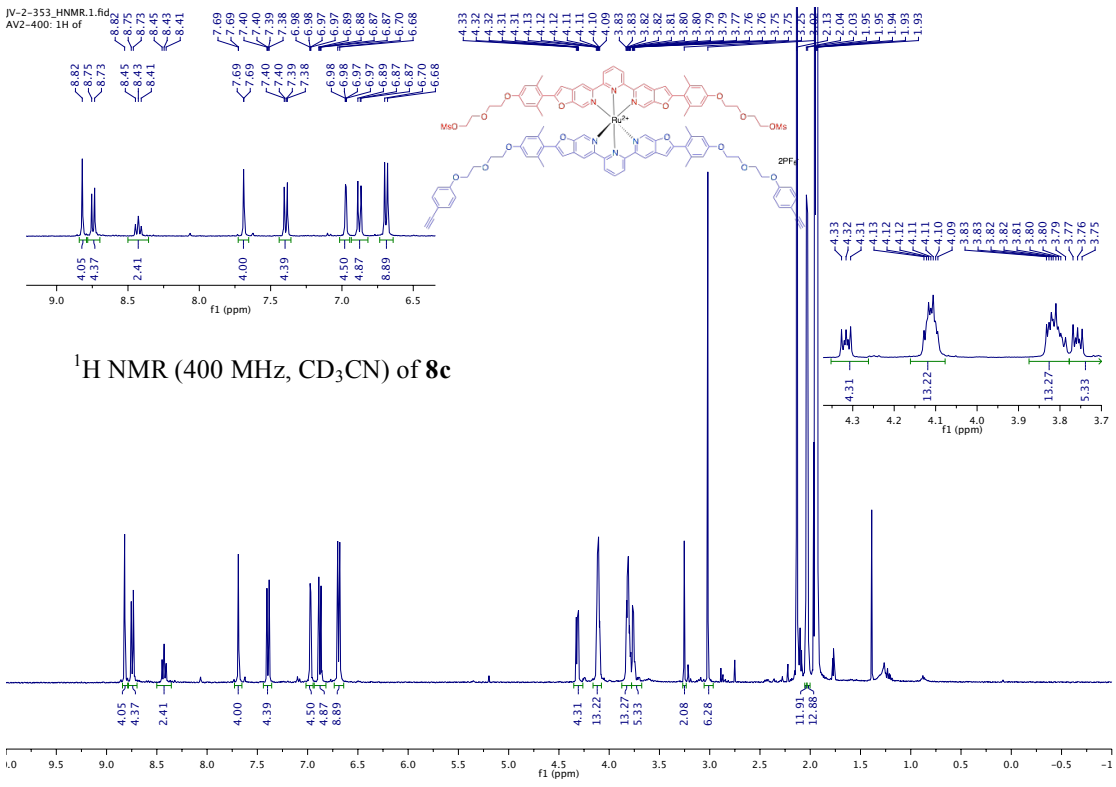


^{13}C NMR (125 MHz, CD_3CN) of **8b**

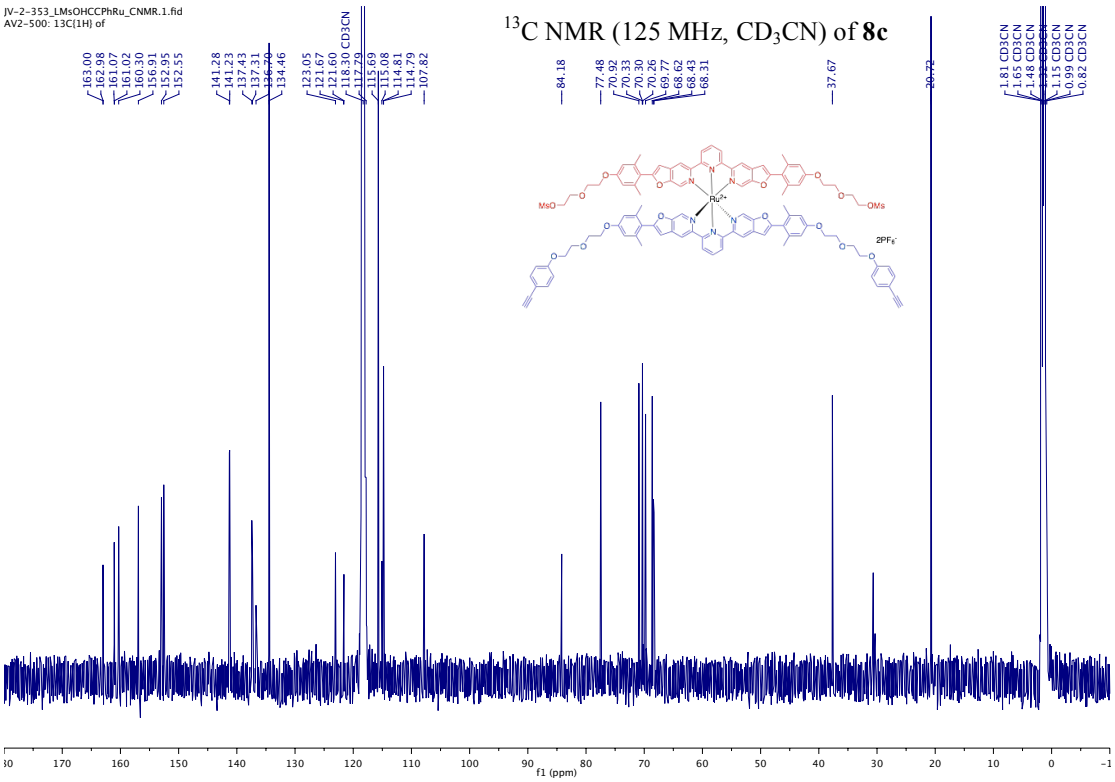


DEPT135 (125 MHz, CD_3CN) of **8b**

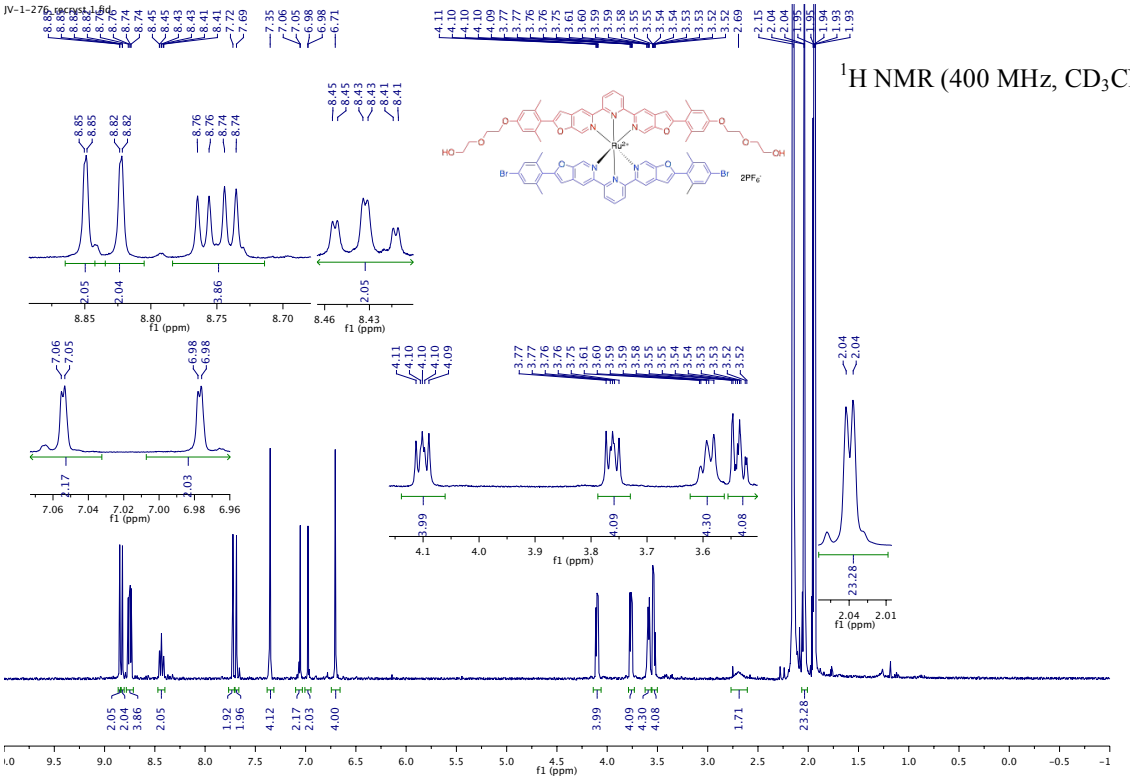




^{1}H NMR (400 MHz, CD_3CN) of **8c**

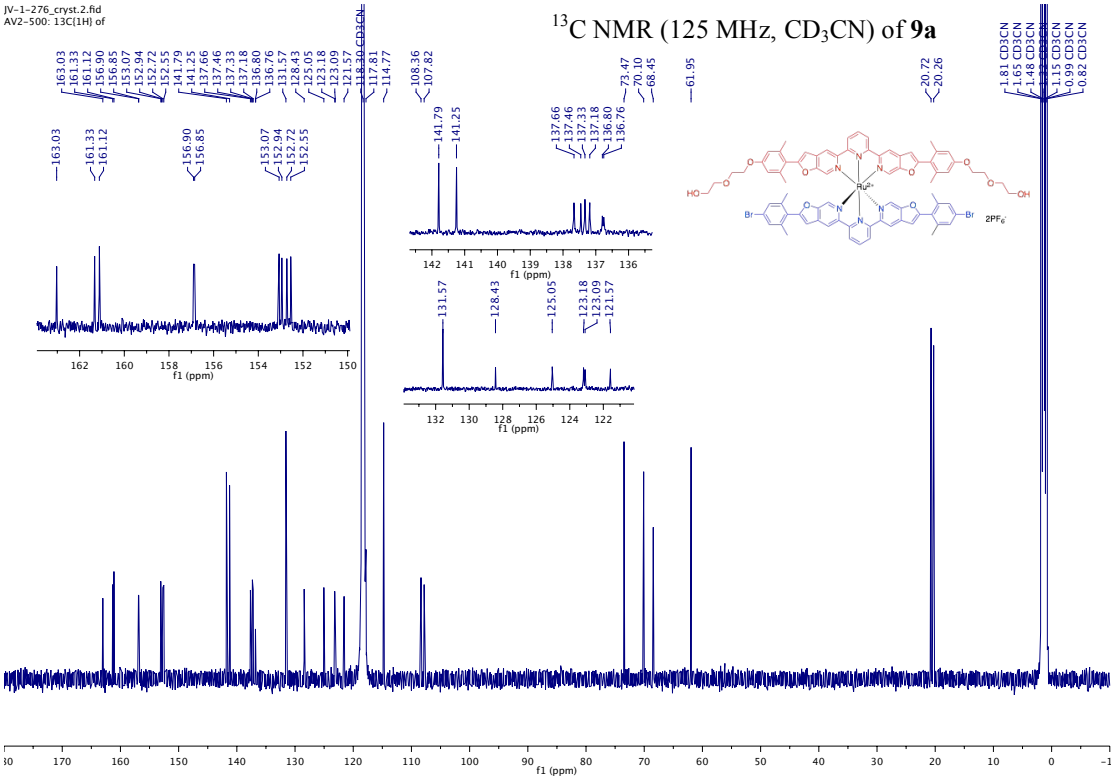


^{13}C NMR (125 MHz, CD_3CN) of **8c**

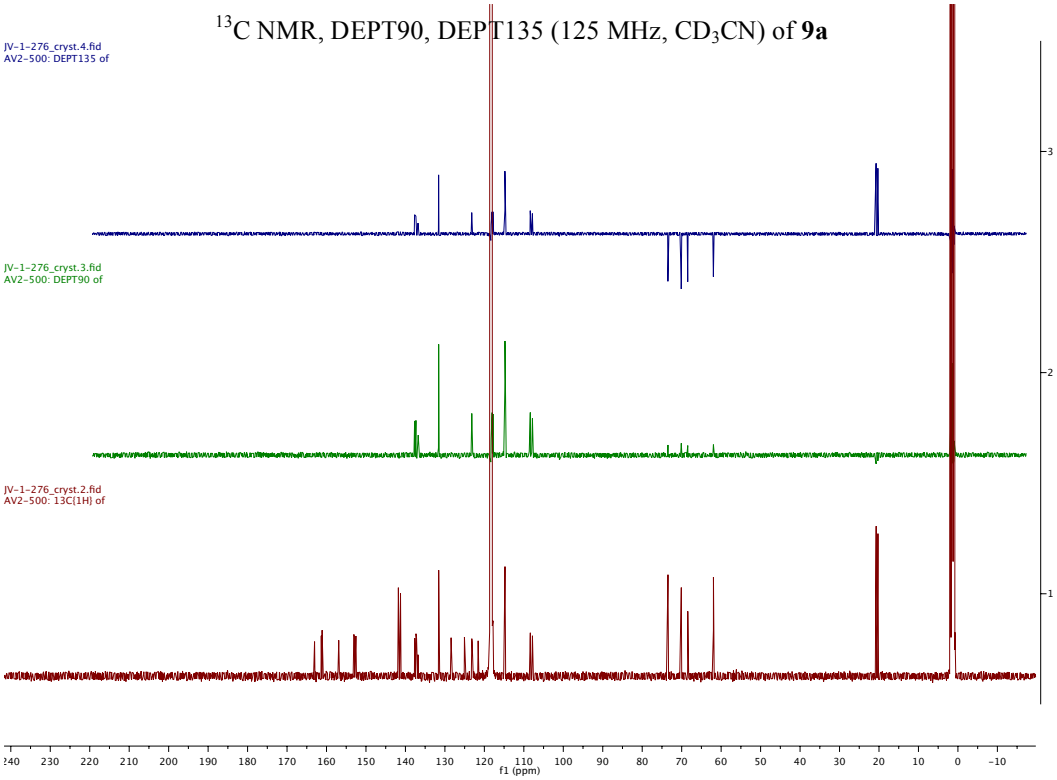


^{1}H NMR (400 MHz, CD_3CN) of **9a**

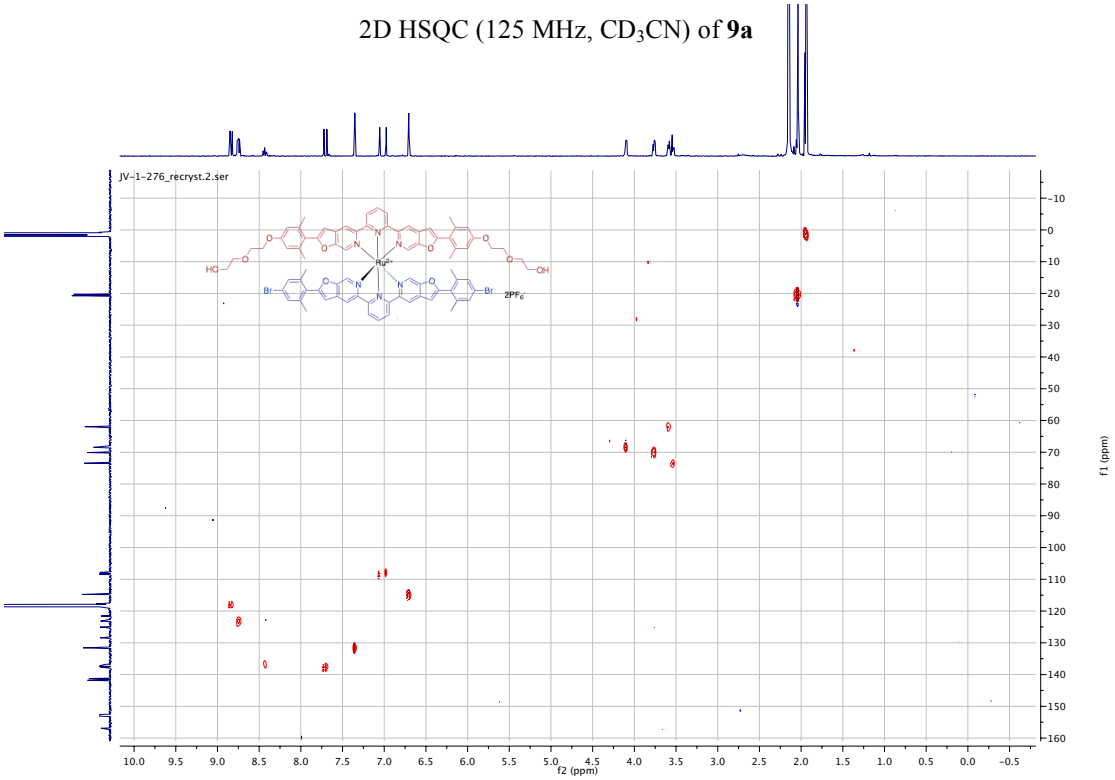
^{13}C NMR (125 MHz, CD_3CN) of **9a**



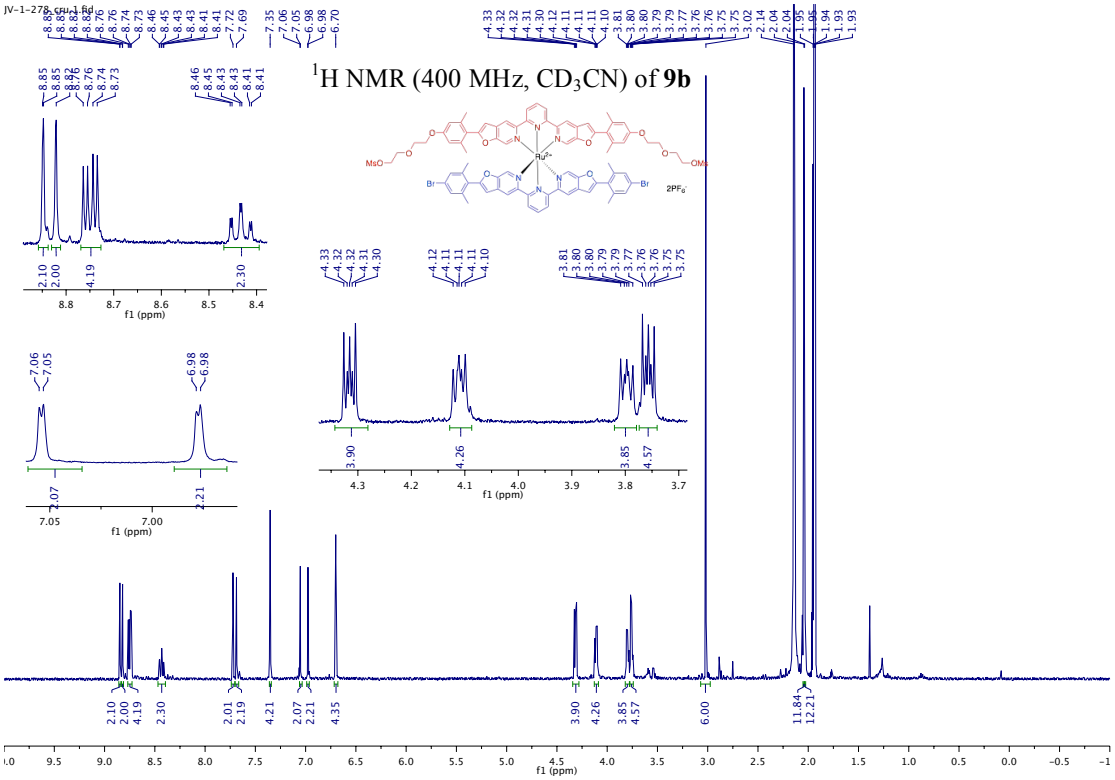
^{13}C NMR, DEPT90, DEPT135 (125 MHz, CD_3CN) of **9a**

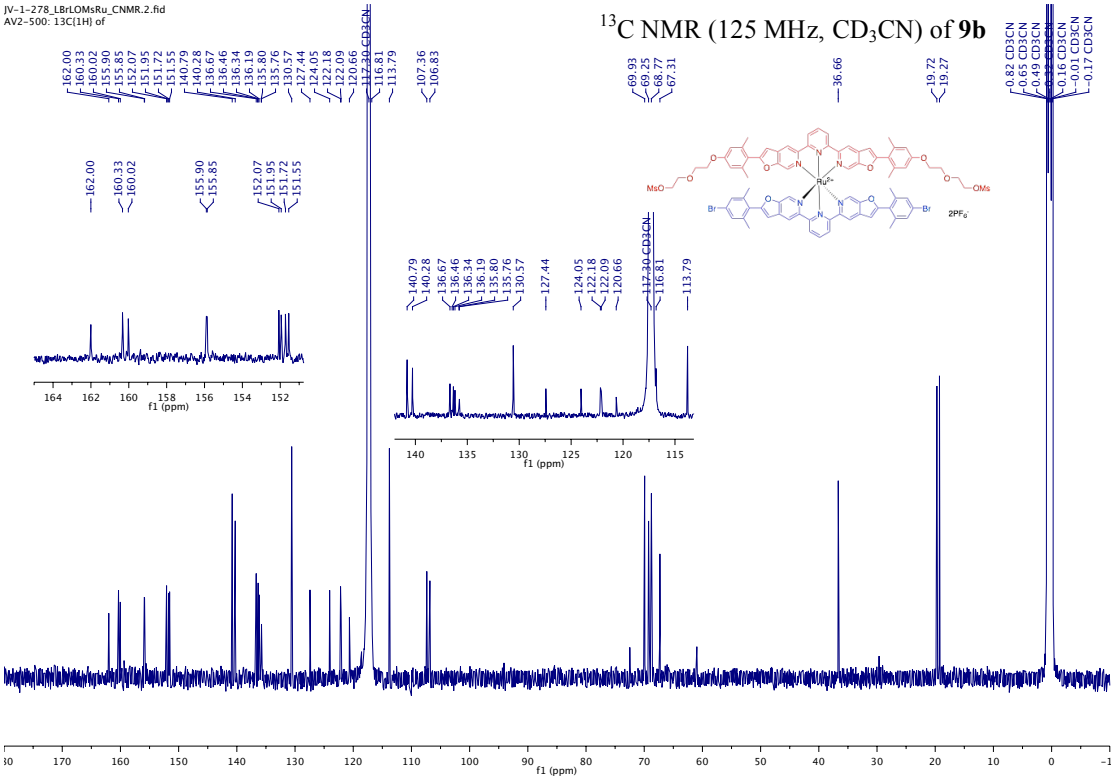


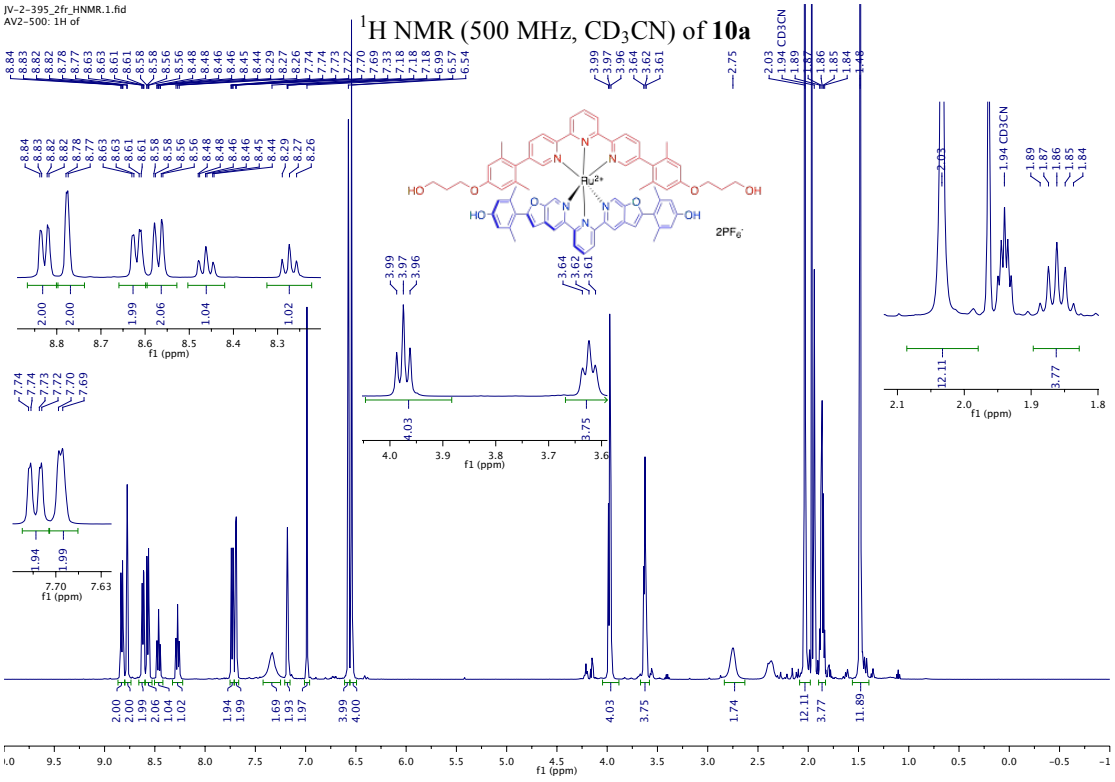
2D HSQC (125 MHz, CD_3CN) of **9a**



^{1}H NMR (400 MHz, CD_3CN) of **9b**




JV-1-278_LBrLOMsRu_CNMR.2.fid
AV2-500: 13C{1H} of
^{13}C NMR (125 MHz, CD$_3$CN) of **9b**
f1 (ppm)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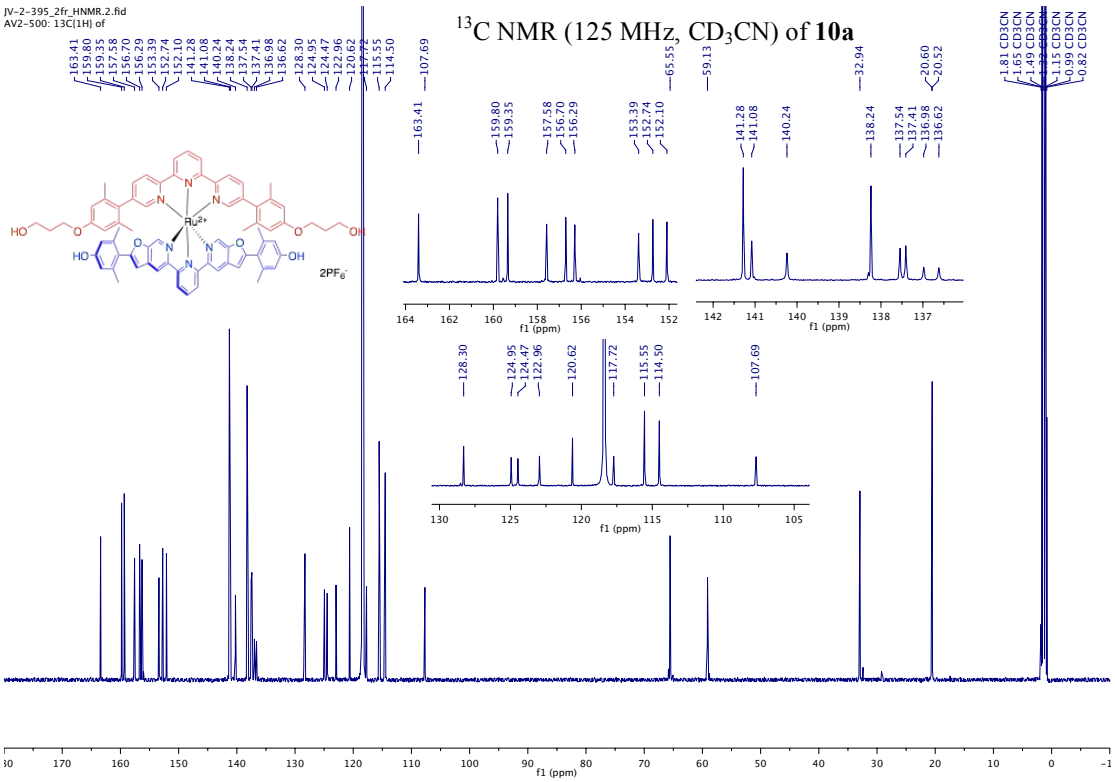
AV2-500: 1H of
^{1}H NMR (500 MHz, CD$_3$CN) of **10a**
f1 (ppm)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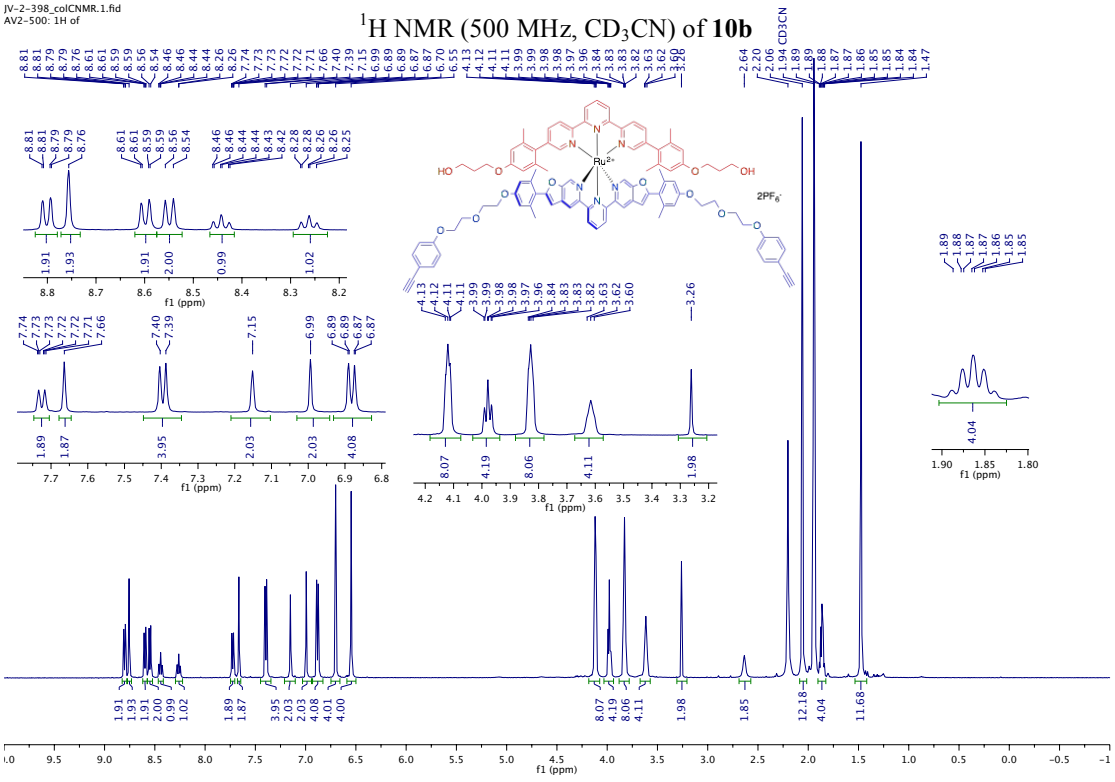
AV2-500: 13C{1H} of
^{13}C NMR (125 MHz, CD$_3$CN) of **10a**
f1 (ppm)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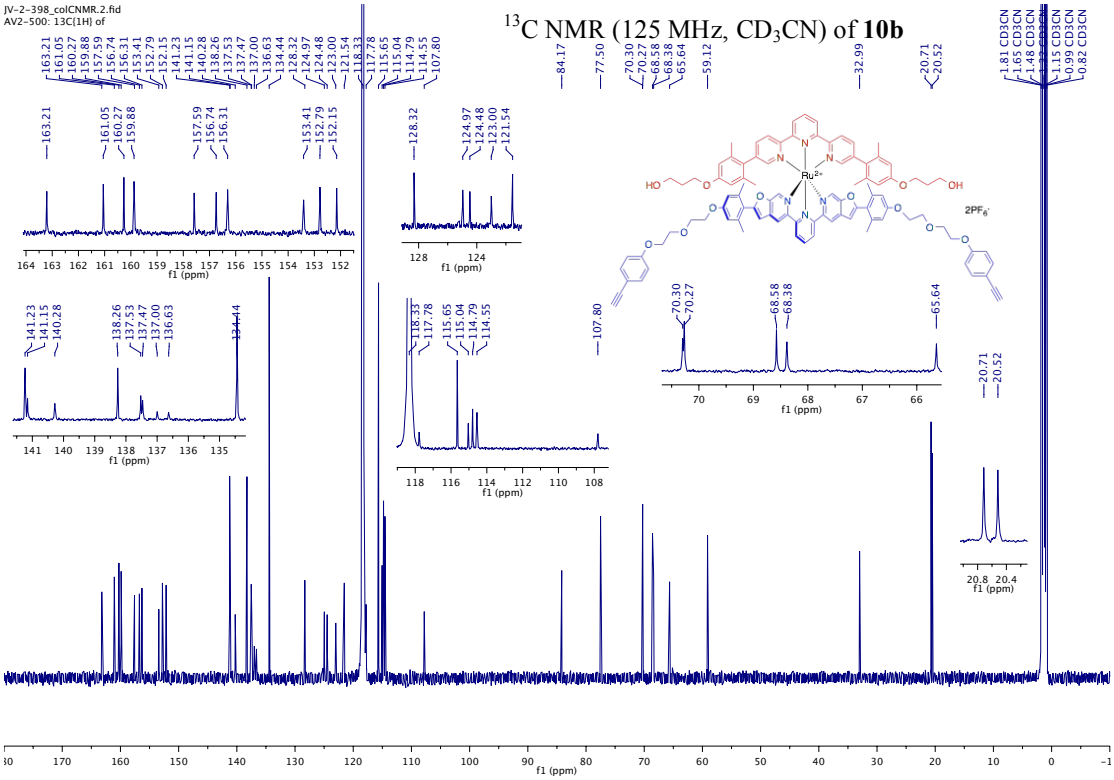
AV2-500: 1H of
^{1}H NMR (500 MHz, CD$_3$CN) of **10b**
f1 (ppm)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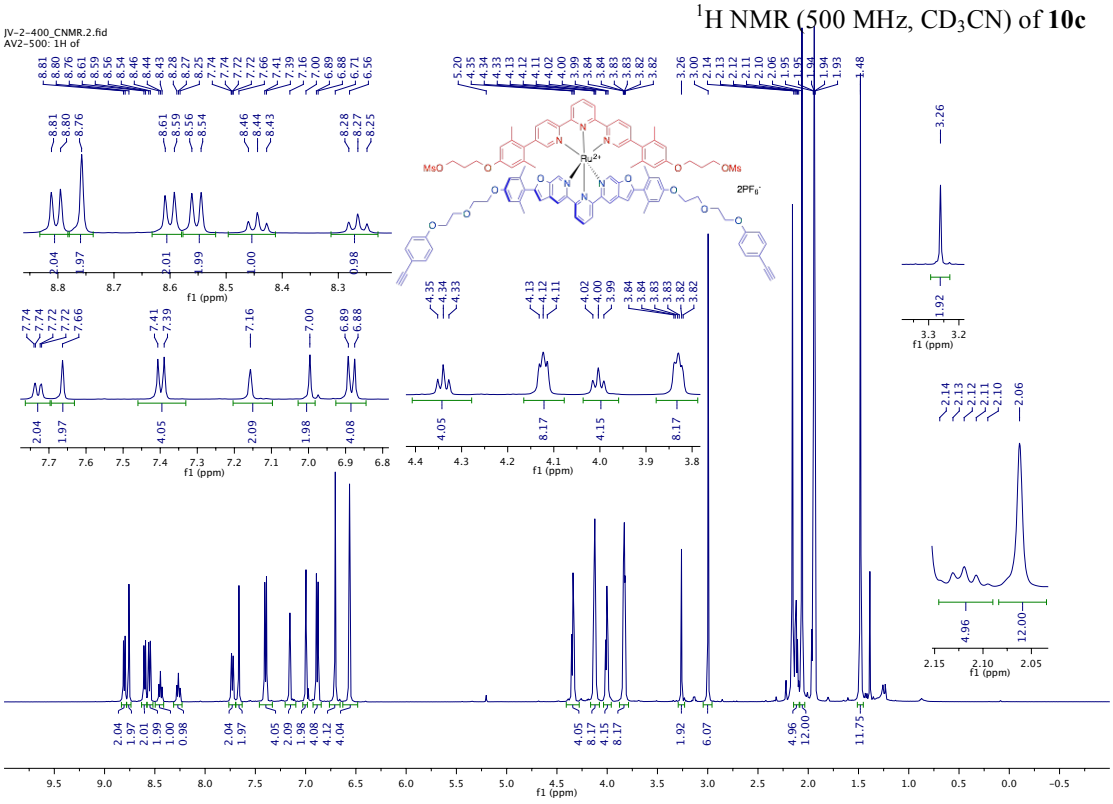
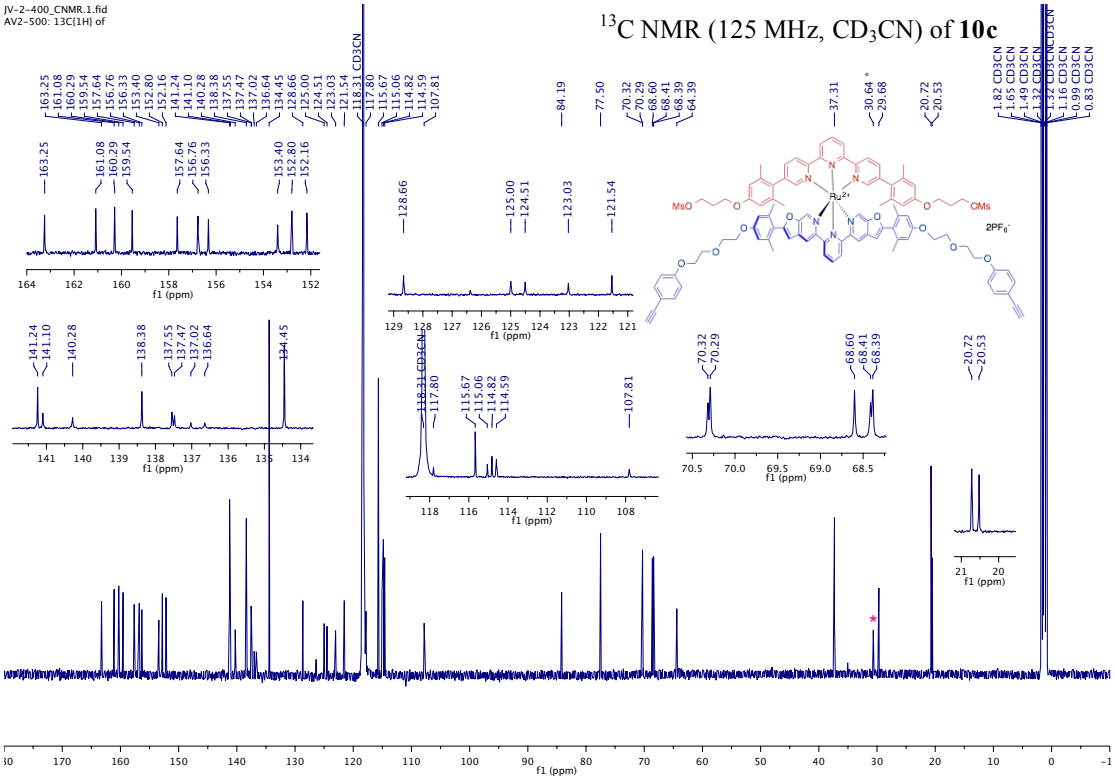
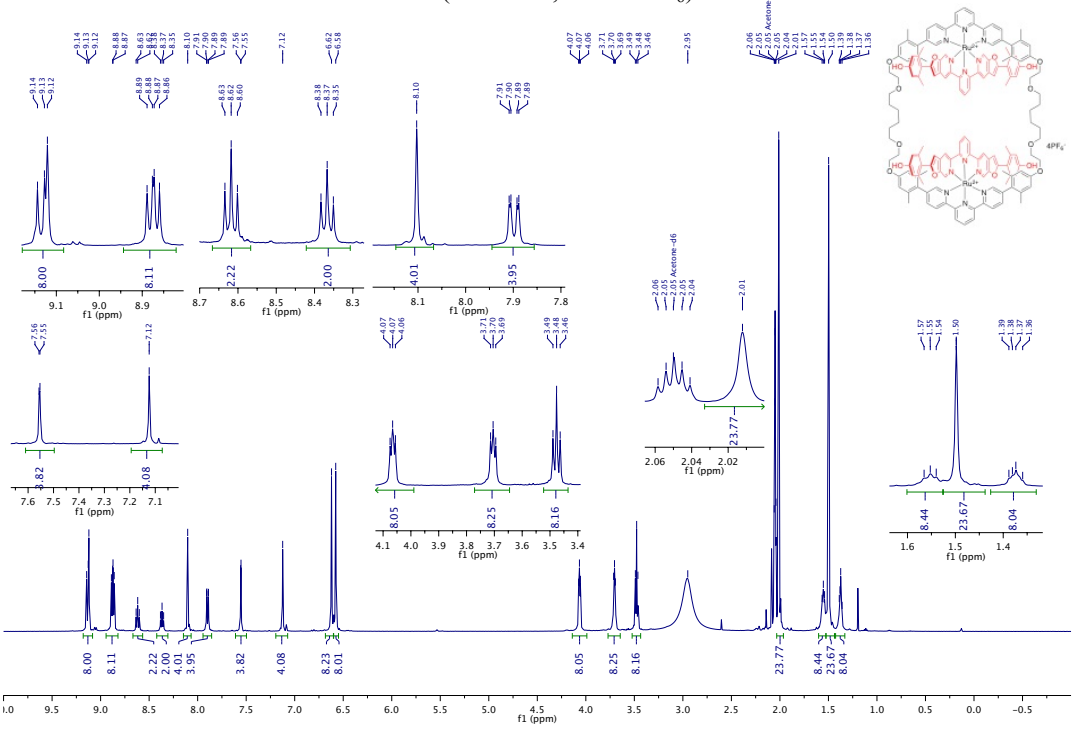
^{13}C NMR (125 MHz, CD$_3$CN) of **10b**
HO
OH
2PF$_6^-$
f1 (ppm)


JV-2-400_CNMR.2.fid
AV2-500: 1H of
^{1}H NMR (500 MHz, CD$_3$CN) of **10c**
MsO
OMs
2PF$_6^-$
f1 (ppm)

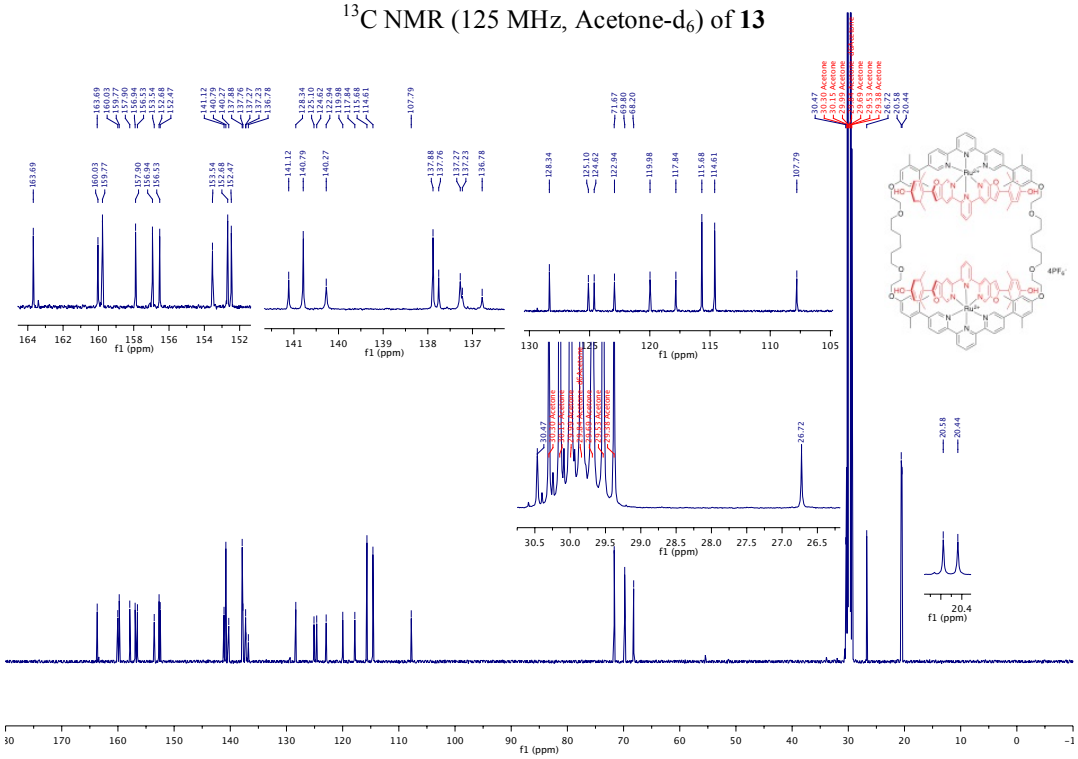
^{13}C NMR (125 MHz, CD_3CN) of **10c**



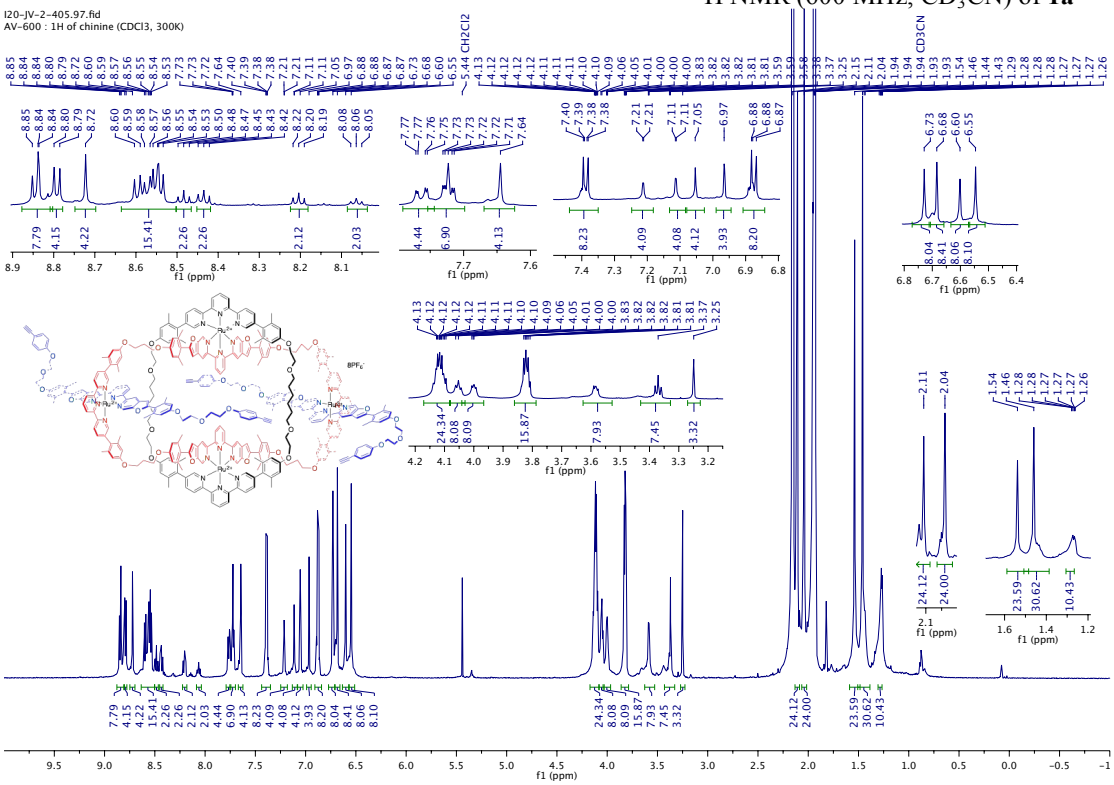
^{1}H NMR (500 MHz, Acetone-d_6) of **13**



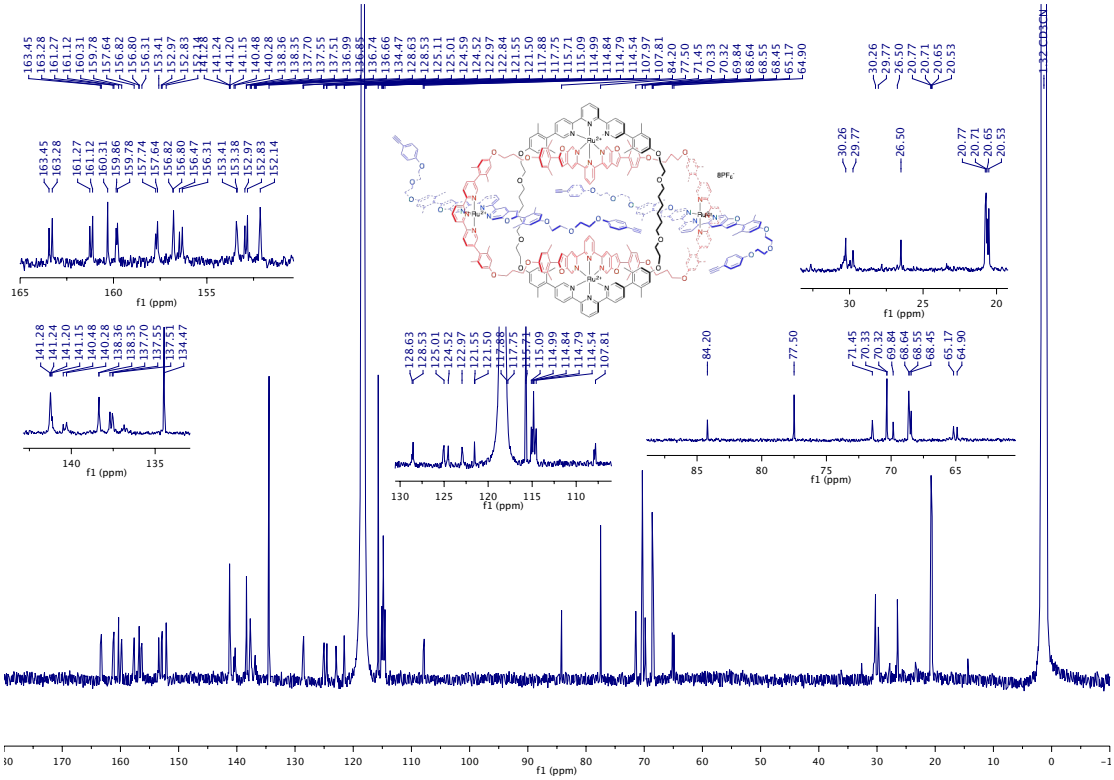
^{13}C NMR (125 MHz, Acetone-d$_6$) of **13**



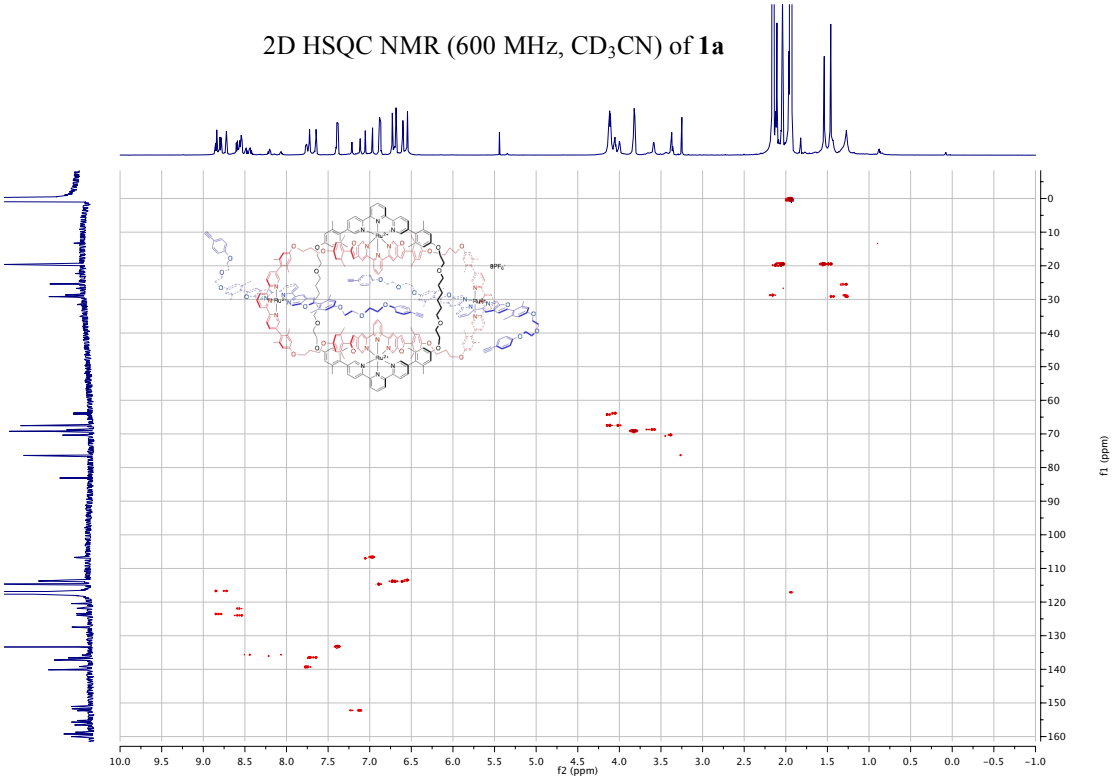
^{1}H NMR (600 MHz, CD$_3$CN) of **1a**

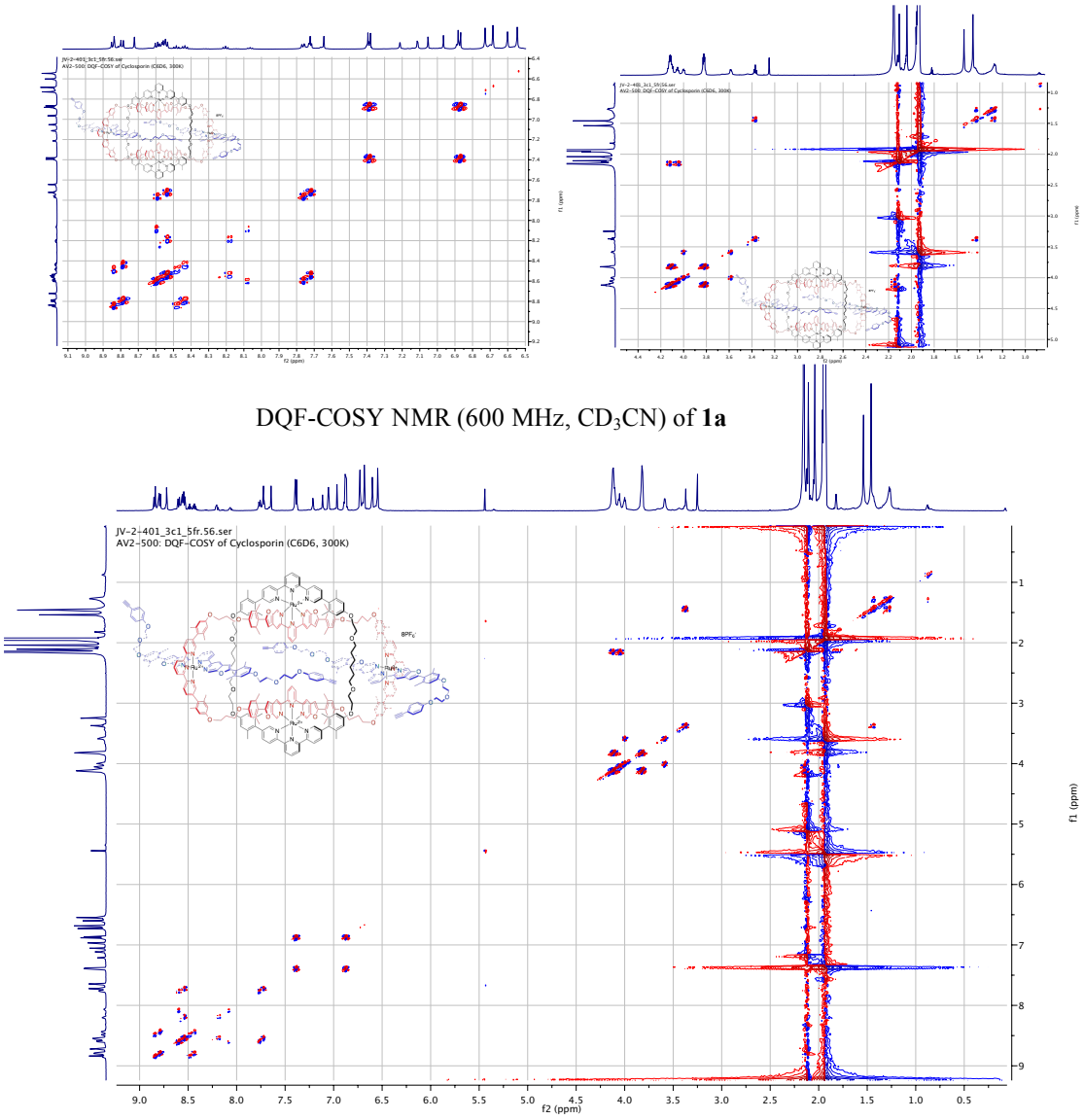


^{13}C NMR (150 MHz, CD_3CN) of **1a**

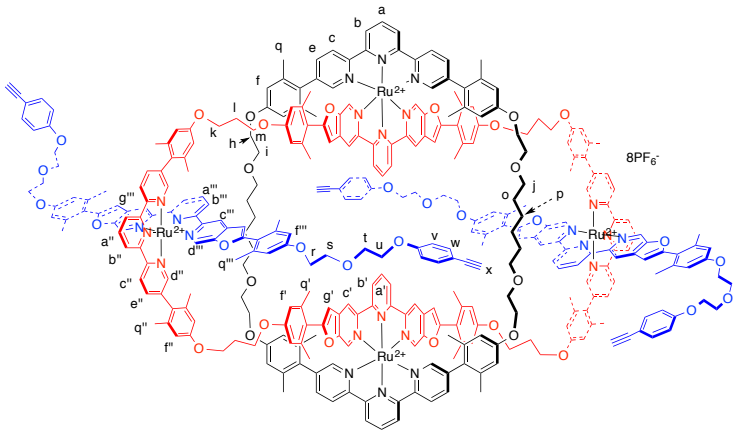


2D HSQC NMR (600 MHz, CD_3CN) of **1a**

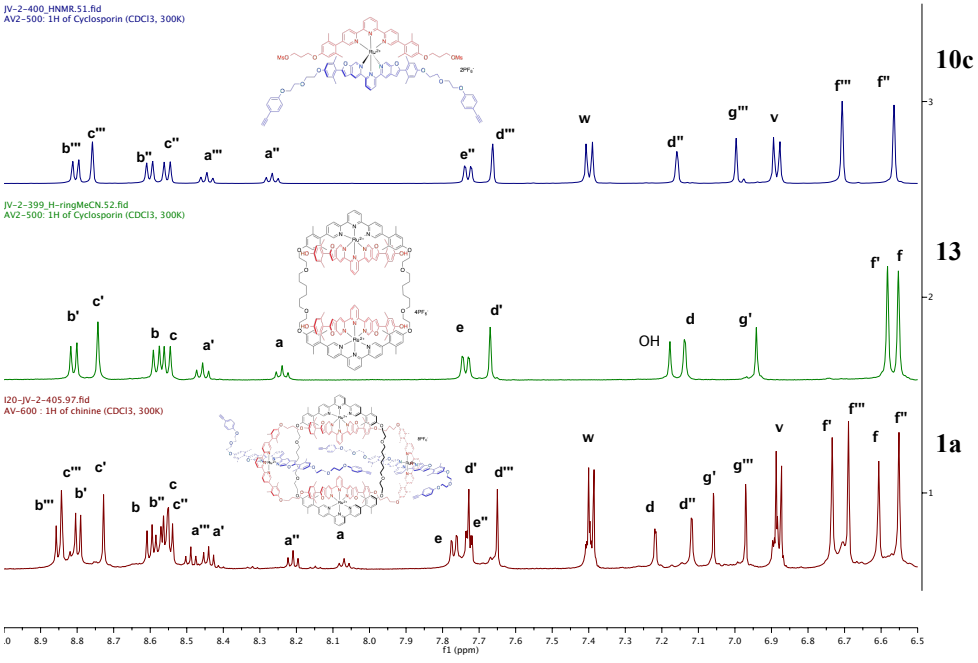


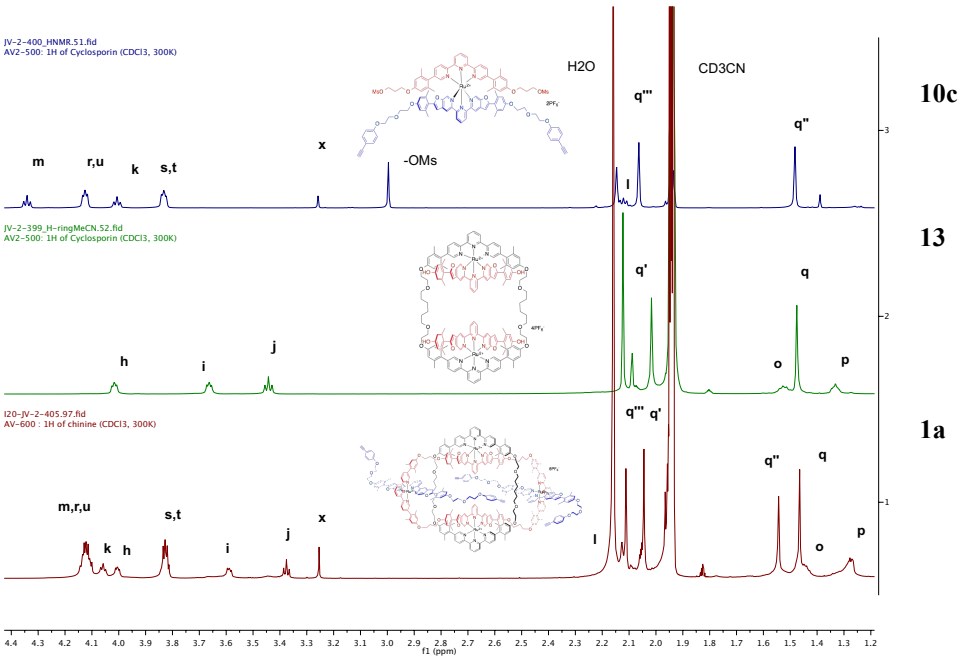


DQF-COSY NMR (600 MHz, CD_3CN) of **1a**



Comparison of ^{1}H NMR spectra of **1a**, **13**, and **10c**





HR-ESI-MS spectrum of **1a**

HR-ESI-MS (Bruker maXis)

Analysis Info

Analysis Name	D:\Data\Service\6190nehres.d	Acquisition Date	5/21/2014 3:32:39 PM
Method	tune_low_modified_09_01_14_pos.m	Operator	ust
Sample Name	JV-2-401	Instrument	maXis 255552.00033
Comment	Solvent: MeCN Client: Veliks		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
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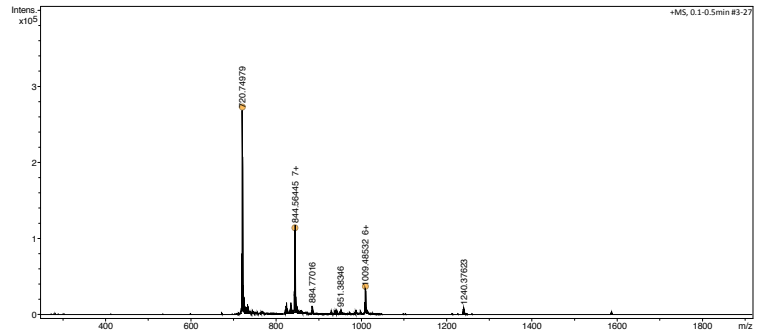
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min



Bruker Compass DataAnalysis 4.2 printed: 5/21/2014 3:49:43 PM by: ust Page1 of 2

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
720.74979	1	C344H316N24O36Ru4	720.74705	-1.26	55.8	1	100.00	201.0	even	ok
844.42169	1	C344H316F6N24O36PRu4	844.42016	0.67	53.1	1	100.00	198.5	even	ok
1009.31875	1	C344H316F12N24O36P2Ru4	1009.31765	1.33	64.7	1	100.00	196.0	even	ok

HR-ESI-MS (Bruker maXis)

Analysis Info

Analysis Name	D:\Data\Service\6190nehres.d	Acquisition Date	5/21/2014 3:32:39 PM
Method	tune_low_modified_09_01_14_pos.m	Operator	ust
Sample Name	JV-2-401	Instrument	maXis 255552.00033
Comment	Solvent: MeCN Client: Veliks		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
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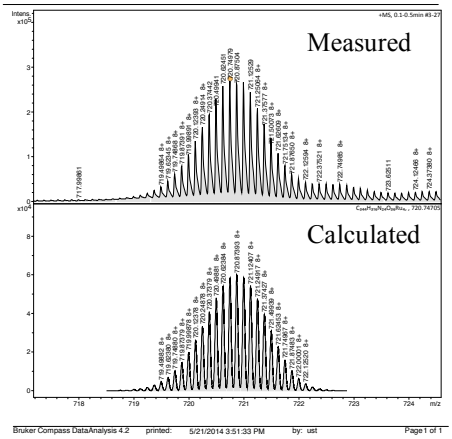
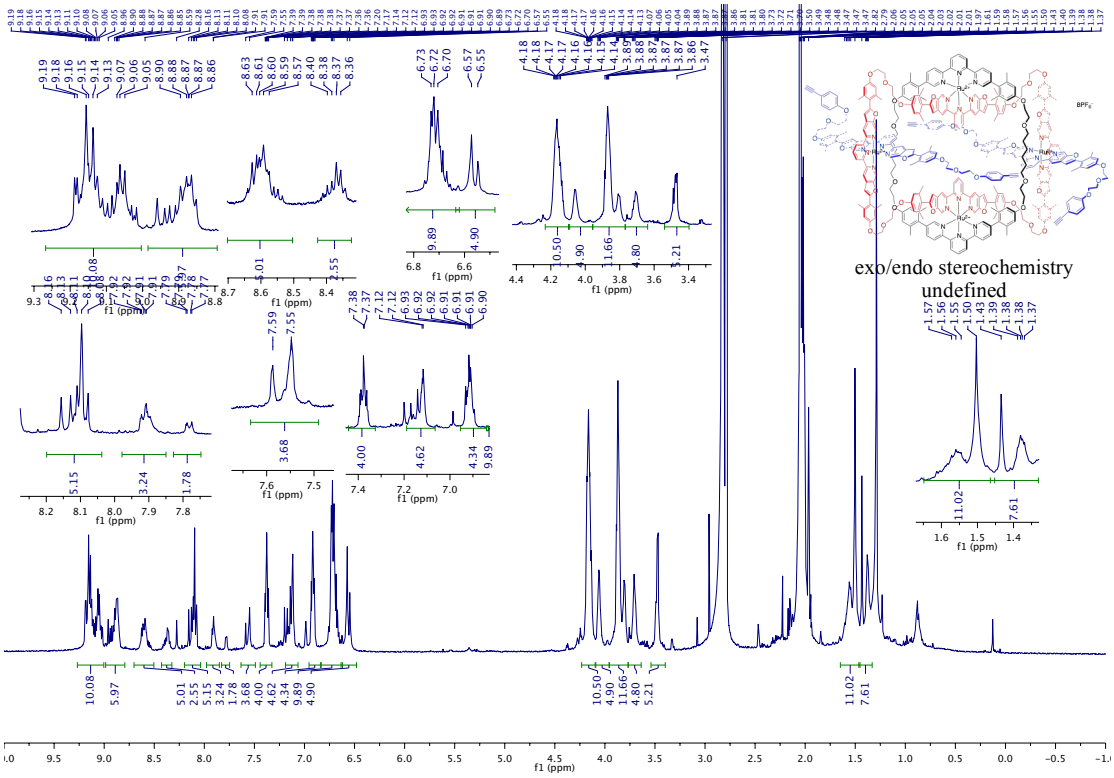
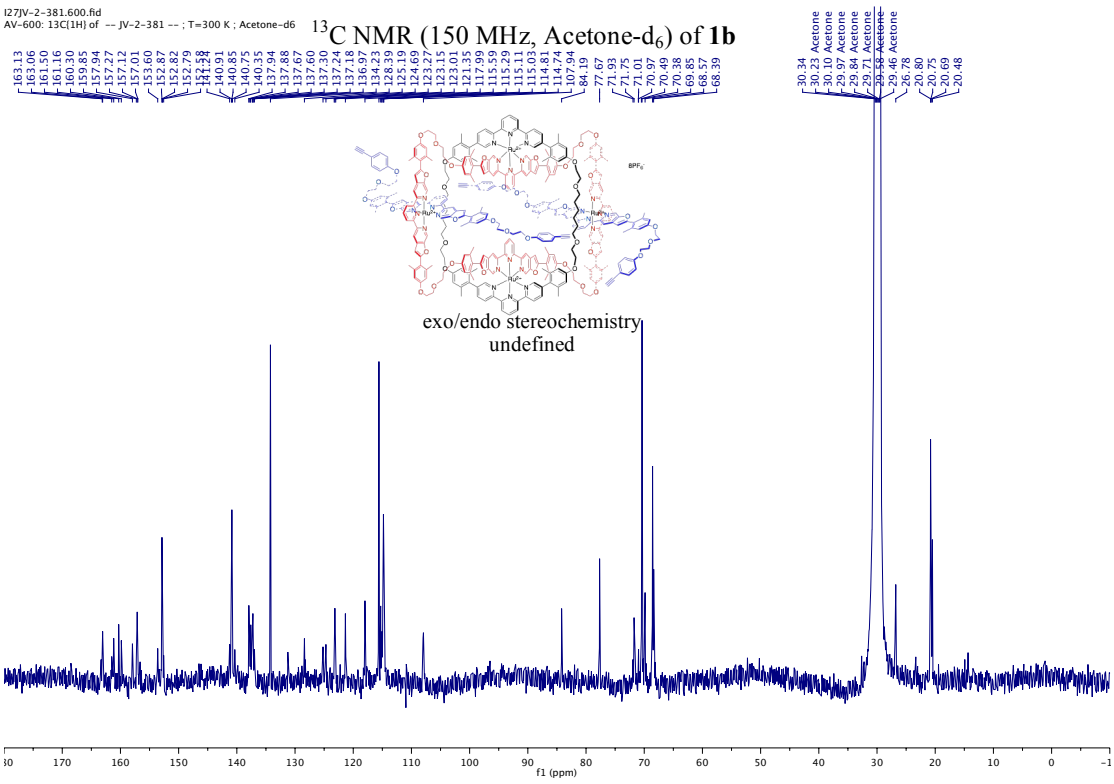


Bruker Compass DataAnalysis 4.2 printed: 5/21/2014 3:51:33 PM by: ust Page1 of 1

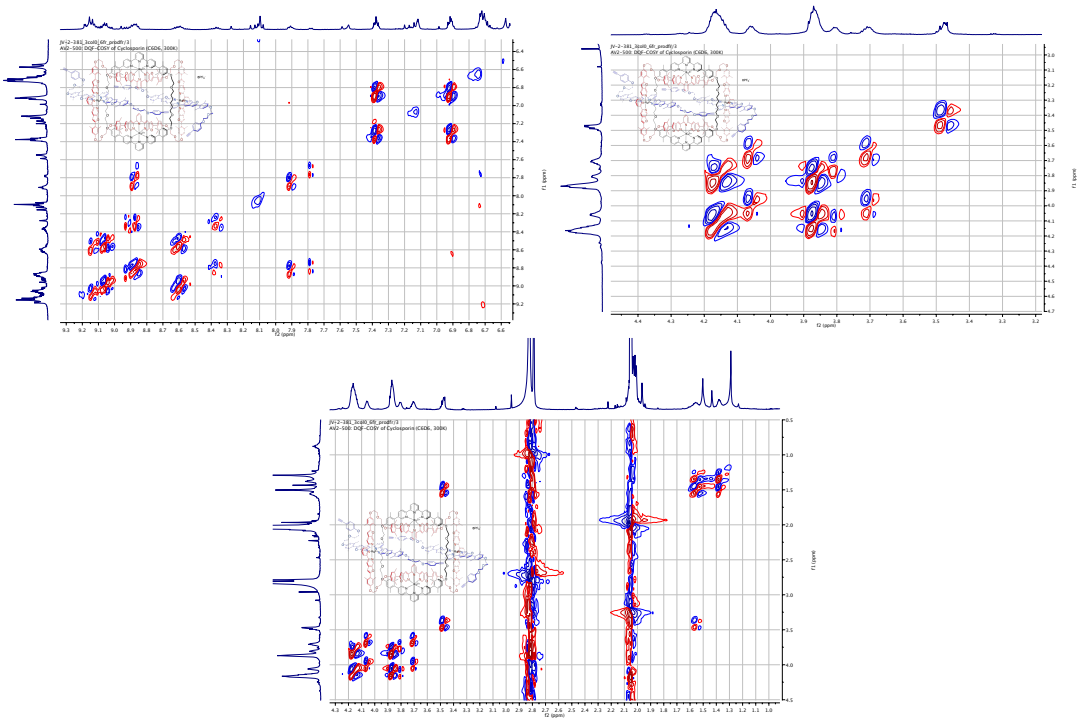
^{1}H NMR (600 MHz, Acetone-d_6) of **1b**



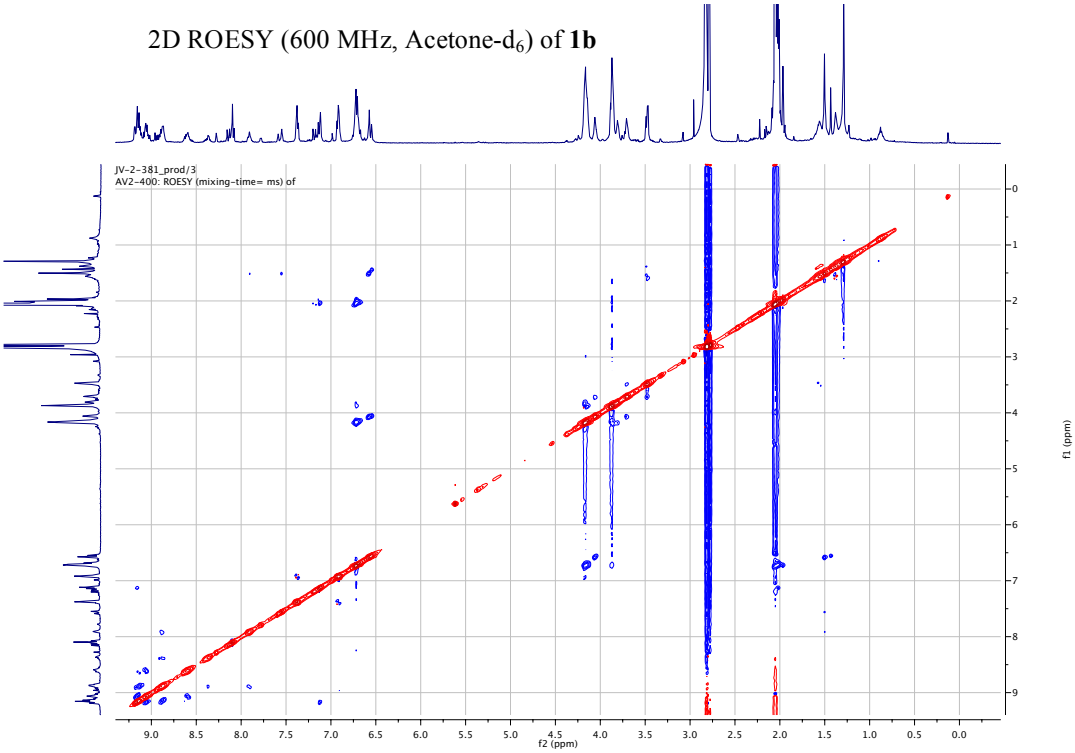


^{13}C NMR (150 MHz, Acetone-d_6) of **1b**

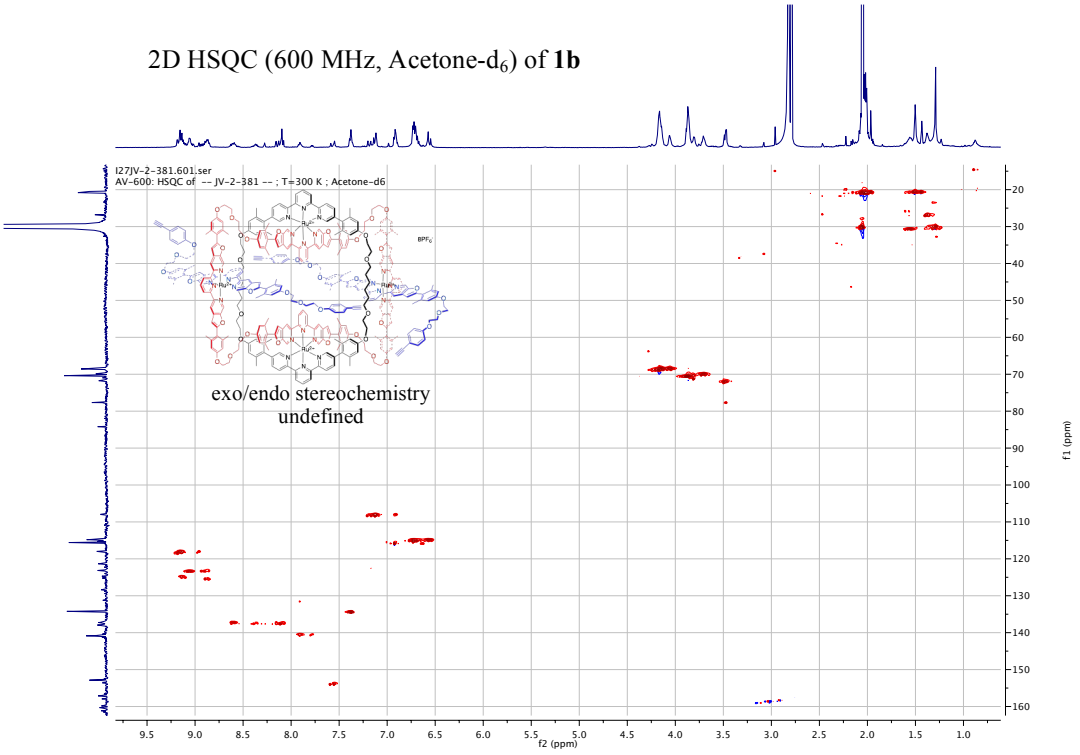
DQF-COSY (600 MHz, Acetone-d_6) of **1b**



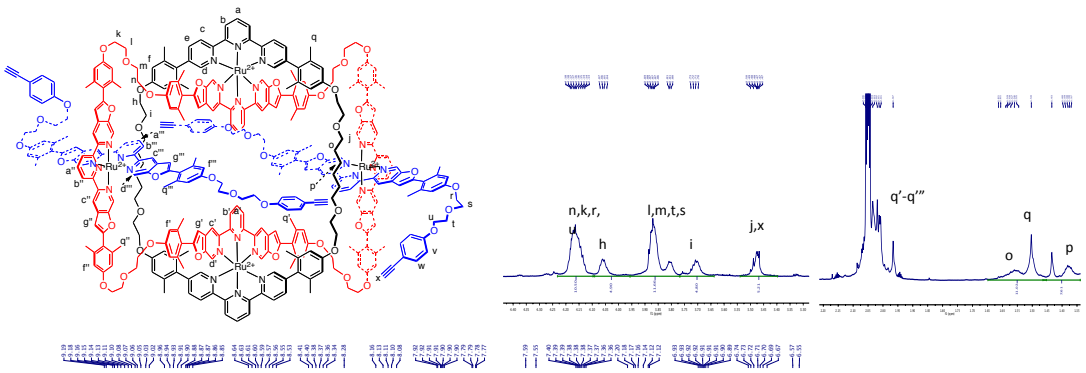
2D ROESY (600 MHz, Acetone-d_6) of **1b**

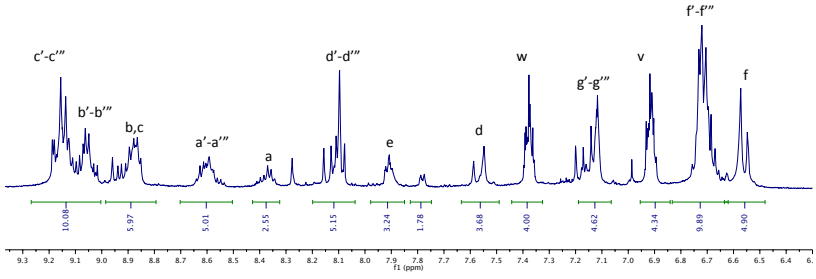


2D HSQC (600 MHz, Acetone-d_6) of **1b**

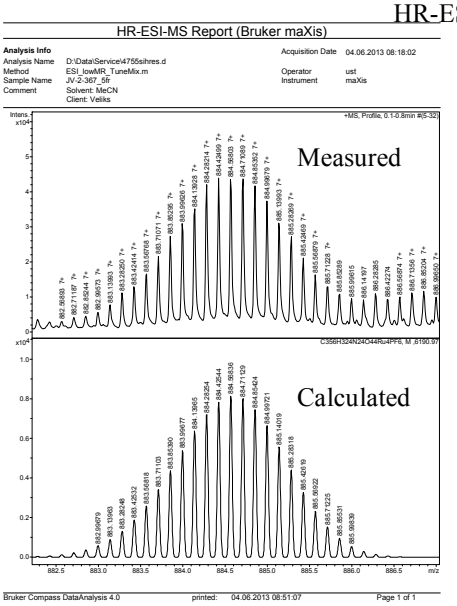


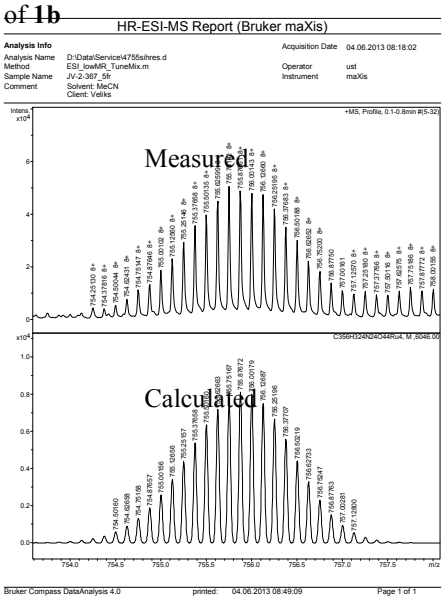
exo/endo stereochemistry
undefined

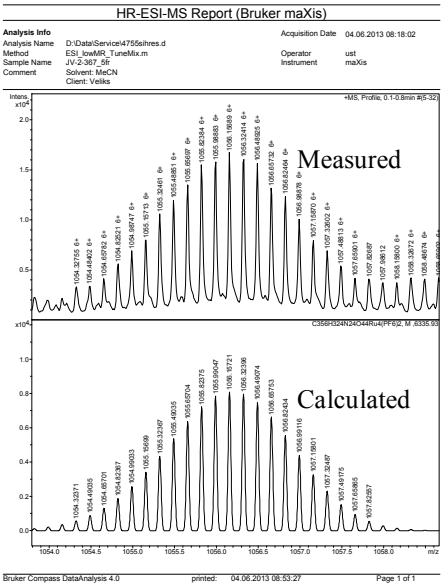




HR-ESI-MS spectrum ~~of **1b**~~





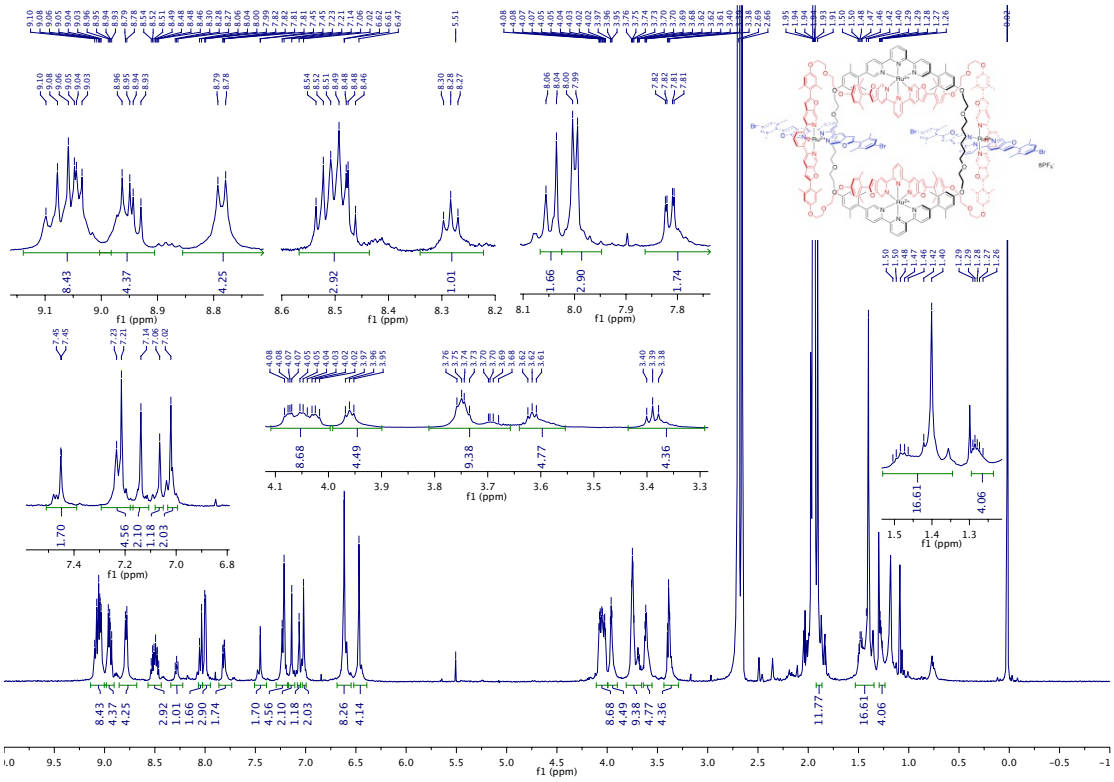


HR-ESI-MS (Bruker maXis)

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
755.75142	1	C 356 H 324 N 24 O 44 Ru 4	100.00	755.75166	0.24	0.32	482.3	209.0	even	ok
884.42499	1	C 356 H 324 F 6 N 24 O 44 P Ru 4	100.00	884.42544	0.44	0.50	475.4	206.5	even	ok
1055.98883	1	C 356 H 324 F 12 N 24 O 44 P 2 Ru 4	100.00	1055.99046	-0.86	-0.82	476.0	204.0	even	ok

^{1}H NMR (600 MHz, Acetone-d_6) of **1c**

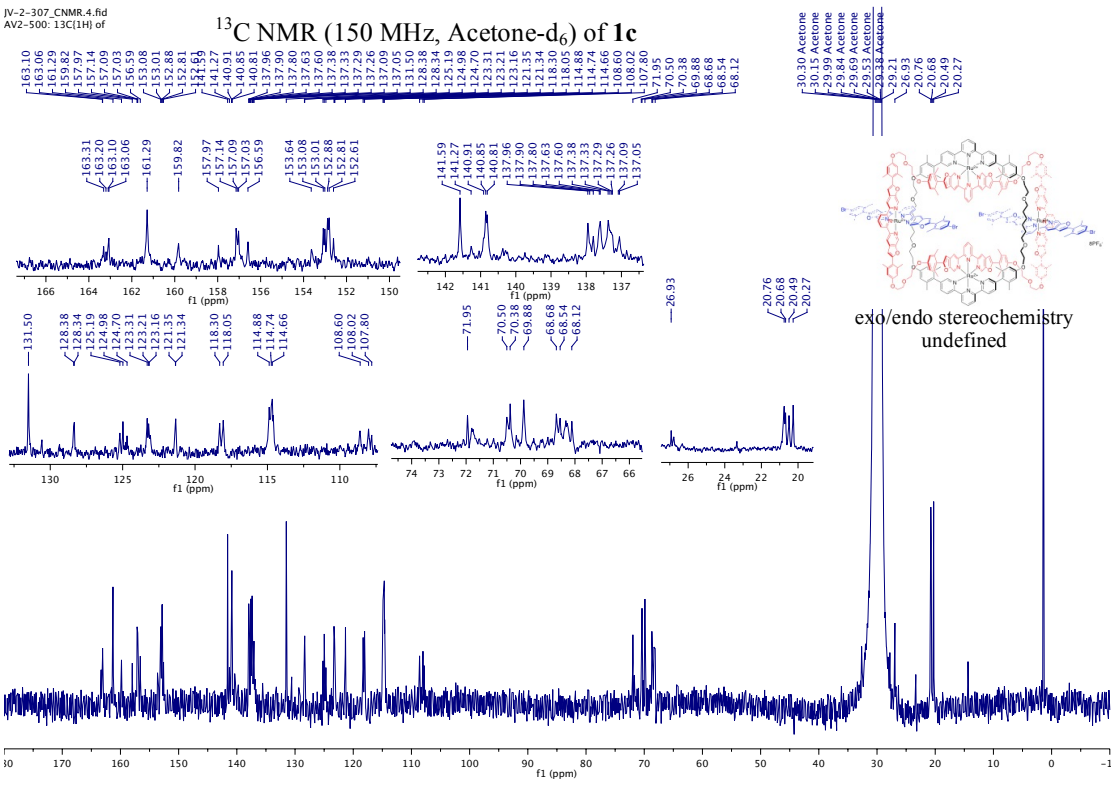
exo/endo stereochemistry undefined



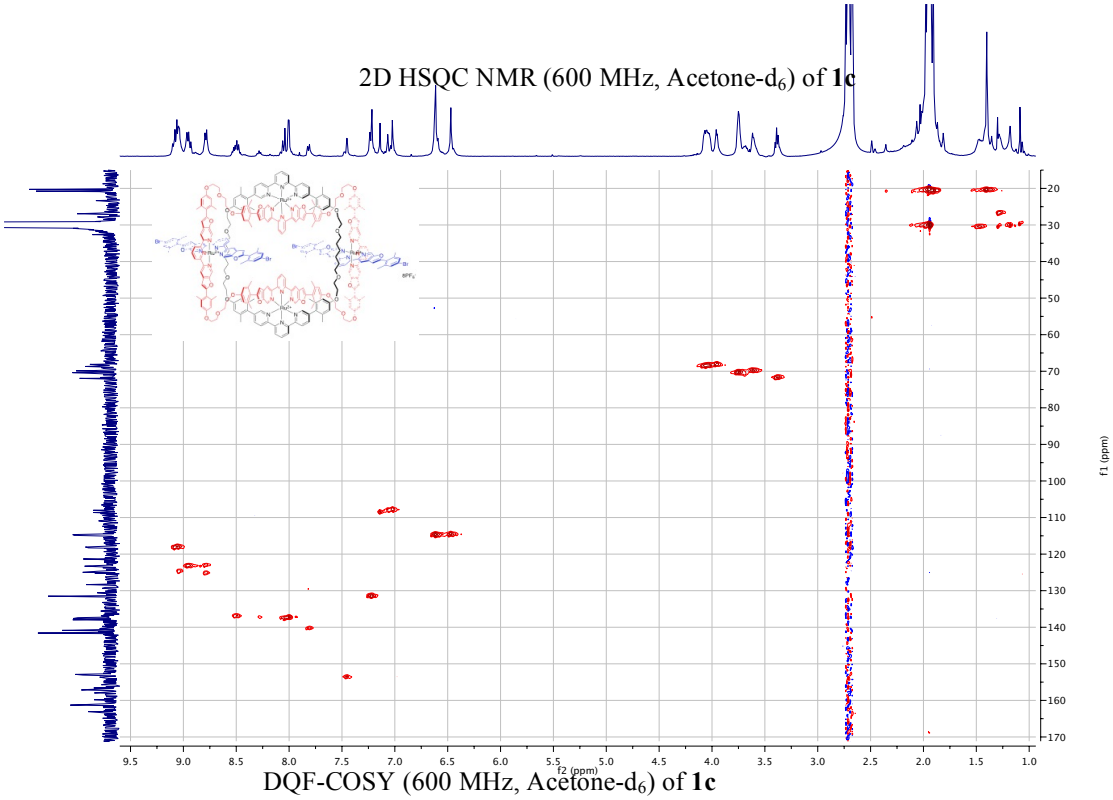
JV-2-307_CNMR.4.fid
AV2-500: 13C{1H} of

^{13}C NMR (150 MHz, Acetone-d_6) of **1c**

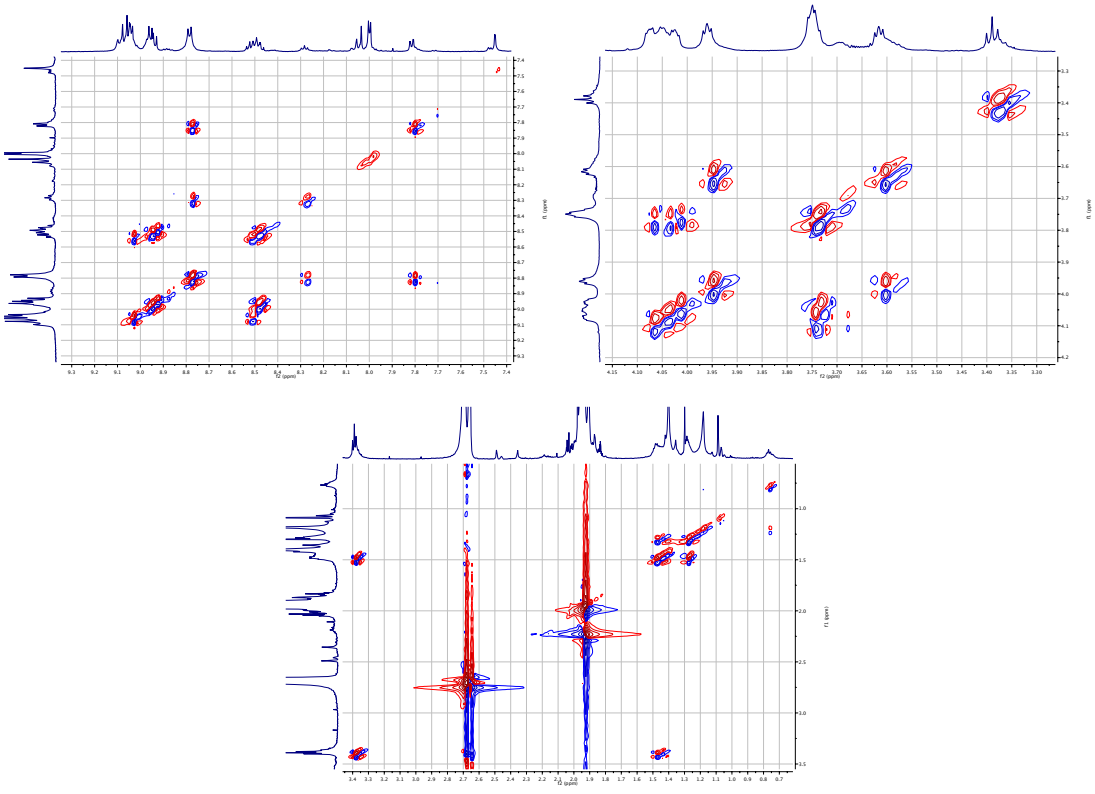
exo/endo stereochemistry undefined

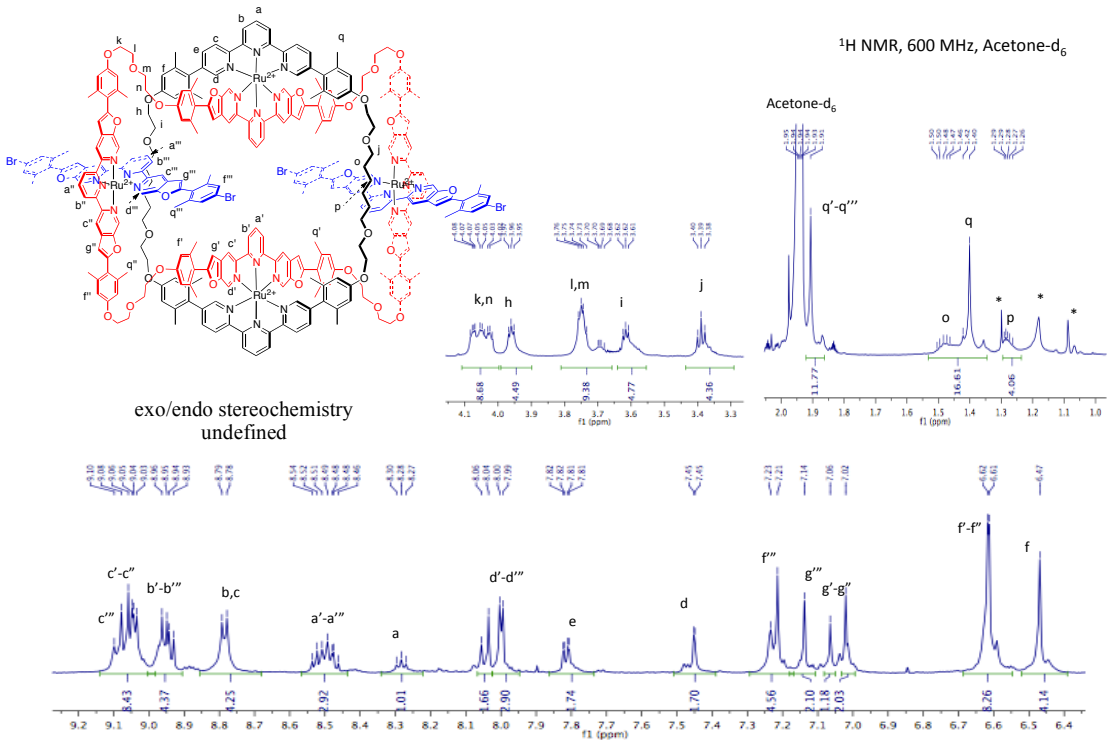


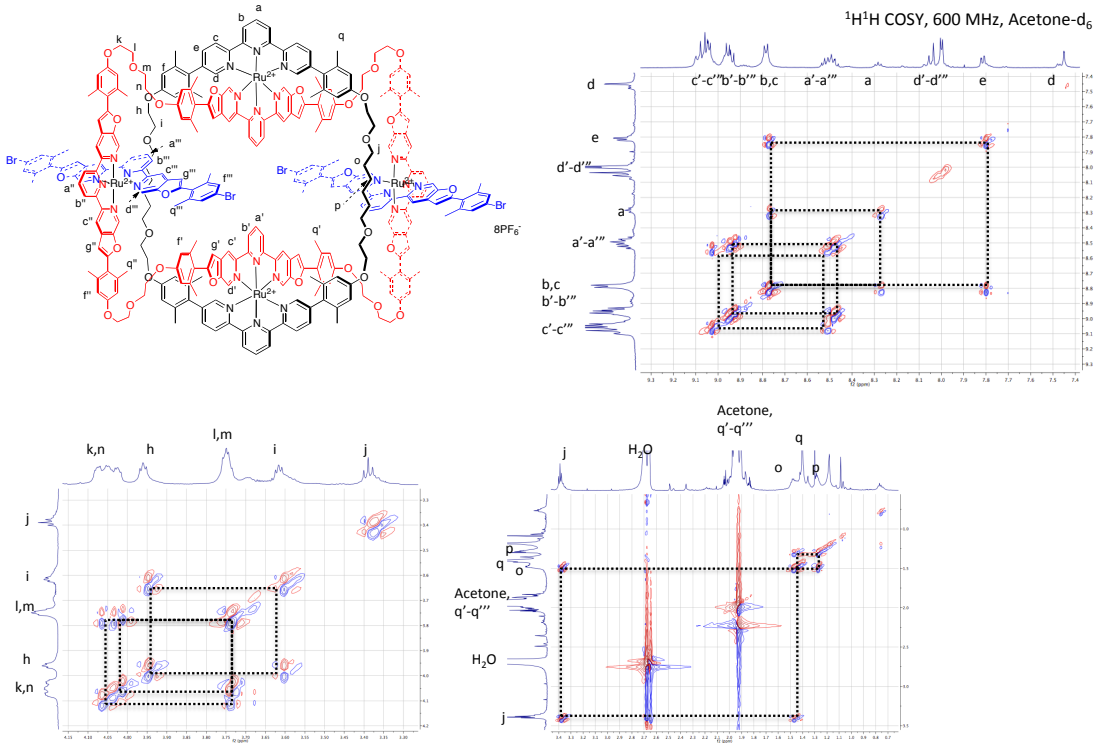
2D HSQC NMR (600 MHz, Acetone-d_6) of **1c**



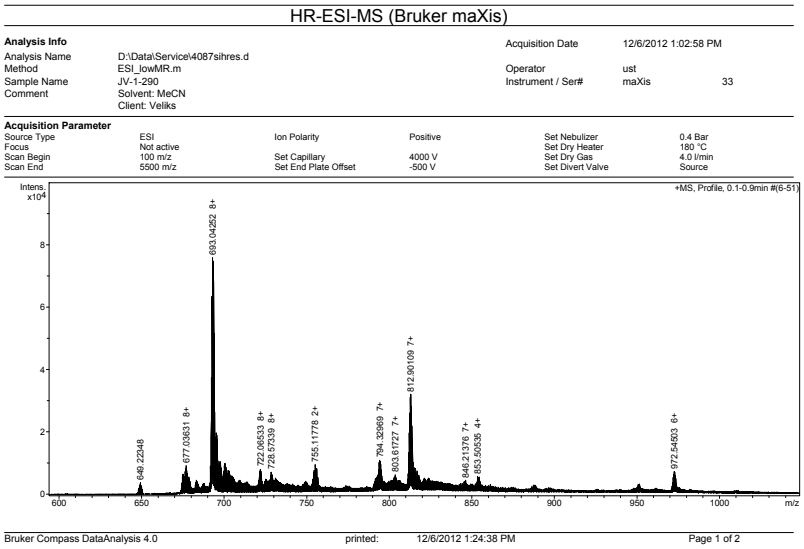
DQF-COSY (600 MHz, Acetone-d_6) of **1c**




exo/endo stereochemistry
undefined
^{1}H NMR, 600 MHz, Acetone-d$_6$
Acetone-d$_6$
k,n
h
l,m
i
j
q'-q'''
q
o
p
c'-c''
b'-b'''
b,c
a'-a'''
a
d'-d'''
e
d
f'''
g'''
g'-g''
f'-f''
f
f1 (ppm)


8PF$_6^-$
^{1}H^{1}H COSY, 600 MHz, Acetone-d$_6$
Acetone,
q'-q'''
H$_2$O

HR-ESI-MS spectrum of **1c**



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
692.66787	1	C 308 H 272 Br 4 N 24 O 32 Ru 4	100.00	692.66692	-0.95	-1.38	497.4	185.0	even	ok
812.32970	1	C 308 H 272 Br 4 F 6 N 24 O 32 P Ru 4	100.00	812.32858	-0.75	-0.93	497.9	182.5	even	ok